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Evaluation of Chemical Reaction Mechanisms for Photochemical Smog. Part 3. Sensitivity of EKMA (Empirical Kinetic Modeling Approach) to Chemical Mechanism and Input Parameters

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16. ABSTRACT

Six chemical reaction mechanisms for photochemical smog were used to study the effect of input parameters on volatile organic compound (VOC) control requirements needed to reduce ozone. The parameters studied were initial VOC composition, dilution rate, post 8-A.M. emissions, base case (present day) O_3 levels, entrainment from aloft of VOC and ozone, initial HONO and initial VOC/NO_x ratio. The Empirical Kinetic Modeling Approach (EKMA) was used to generate ozone isopleths for each chemical mechanism. The VOC control needed to reduce the maximum ozone concentration from some present day value to 0.12 ppm was calculated using the six mechanisms. The initial VOC/NO_x ratio was found to have the largest effect of all the parameters studied on VOC control requirements. Ozone entrainment from aloft and the composition of the initial VOC mixture also had a large effect on predicted control requirements. To reduce the degree of uncertainty in control predictions, it is necessary to establish as accurately as possible the composition of urban air. Also, because of the substantial effect the choice of chemical mechanism has on predicted control requirements, it is important that efforts continue to be directed toward evaluating candidate mechanisms with respect to their ability to simulate atmospheric smog chemistry.

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EVALUATION OF CHEMICAL REACTION MECHANISMS FOR PHOTOCHEMICAL SMOG

Part III. Sensitivity of EKMA to Chemical Mechanism and Input Parameters

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ABSTRACT

The six chemical reaction mechanisms for photochemical smog described in Parts I and II (McRae et al., 1983; Leone and Seinfeld, 1983) were used to study the effect of input parameters on volatile organic compound (VOC) control requirements needed to meet the National Ambient Air Quality Standard for ozone. The parameters studied were initial VOC composition, dilution rate, post 8-A.M. emissions, base case (present day) O_3 levels, entrainment from aloft of VOC and ozone, initial HONO and initial VOC/NO_x ratio. The Empirical Kinetic Modeling Approach (EKMA) was used to generate ozone isopleths for each chemical mechanism. The VOC control needed to reduce the maximum ozone concentration from some present day value to 0.12 ppm, assuming no NO_x control and a specified initial VOC/NO_x ratio, was calculated using the six chemical reaction mechanisms. The initial VOC/NO_x ratio was found to have the largest effect of all the parameters studied on VOC control requirements. Choice of chemical mechanism, ozone entrainment from aloft and the composition of the initial VOC mixture also had a large effect on predicted control requirements. To reduce the degree of uncertainty in control predictions using EKMA it is necessary to establish as accurately as possible the composition of urban air in early morning. Also, because of the substantial effect the choice of chemical mechanism has on the predicted control requirements using EKMA, it is important that future work continue to be directed toward evaluating candidate chemical mechanisms with respect to their ability to simulate atmospheric smog chemistry.

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1. INTRODUCTION

Currently there are several chemical reaction mechanisms available for use in predicting hydrocarbon and NO_x reductions needed to meet the National Ambient Air Quality Standard (NAAQS) for ozone for a particular region. Because of the numerous organic species in the atmosphere, it is computationally infeasible to use a chemical reaction mechanism that contains every reaction of every species in carrying out a control calculation. Each chemical mechanism reduces the number of organic species in a somewhat different way. This reduction, or "lumping," would not be a concern if each of the chemical mechanisms gave similar predictions under typical atmospheric conditions. As discussed in Part II, however, several investigators (Carter et al., 1982; Dunker et al., 1984; Gipson, 1983a, 1983b; Jeffries et al., 1981; Killus and Whitten, 1984) have shown that different photochemical smog reaction mechanisms predict significantly different control requirements under the same conditions. In addition, these investigators have found that the sensitivity of the mechanism's predictions to changes in input parameters varies among mechanisms. Because of the importance of making intelligent hydrocarbon control decisions, it is necessary to understand in as fundamental way as possible how the choice of chemical mechanism, as well as the choice of input parameters, affects control predictions. The object of this work, therefore, is to present a comprehensive, systematic study of the sensitivity of predicted hydrocarbon control requirements for photochemical smog to the choice of chemical mechanism and choice of all input parameters in the control calculation.

To study the sensitivity of hydrocarbon control predictions to choice of chemical mechanism and input parameters we will use the U.S. Environmental Protection Agency's Empirical Kinetic Modeling Approach (EKMA) in which ozone isopleths

are generated as a function of initial volatile organic compound (VOC) and NO_x concentrations using a chemical reaction mechanism. In the EKMA methodology, a chemical reaction mechanism for photochemical smog is used to predict the maximum ozone concentration achieved over a fixed time of irradiation, say 10 hours, as a function of initial precursor concentrations (VOC and NO_x). The maximum ozone concentrations corresponding to each set of initial concentrations are then represented as isopleths, from which control requirements are obtained graphically by assuming that the reductions in initial concentrations needed to lower the maximum ozone concentration from one isopleth (the base case value) to another (usually the NAAQS of 0.12 ppm) are linearly related to the emissions of each precursor. The chemical reaction mechanism is integrated from early morning, e.g. 0800 hours, to calculate the evolution of species concentrations in a hypothetical air parcel that starts from center city and is advected by the wind. The air parcel may increase in size due to changes in the mixing height and acquire additional pollutants from both fresh source emissions and entrainment of aged pollutants from aloft. The simulations on which the isopleths are based can be performed at two different levels of detail: Level II, which requires a specific meteorological description of the air parcel trajectory and emissions along the trajectory, and Level III, which makes standard assumptions about the meteorology and which uses a region-wide average for emission rates. Killus and Whitten (1984) have shown that the sensitivity of ozone predictions to choice of chemical mechanism does not change appreciably when one imbeds the mechanisms in models that are more sophisticated than the simple Lagrangian box model on which EKMA is based. Therefore, we expect that the results of the current study, which we will obtain by use of EKMA, will be a valid indication of the effects of chemical mechanism and input parameters on predicted organic control requirements regardless of the level of sophistication of

the air quality model in which the mechanism is imbedded.

This report represents the third part of a three-part study of lumped reaction mechanisms for photochemical smog. Part I (McRae et al., 1983) contains information concerning the various approaches to lumping, and how the particular mechanisms chosen for the study were selected. Also included in Part I is a detailed description of each lumped mechanism. Part II (Leone and Seinfeld, 1983) of the study was focused on elucidating the differences among the mechanisms. To do so a so-called counter species analysis was used to ascertain the number of NO to NO_2 conversions attributed to each organic class. Based on the results of the analysis it was possible to identify the specific features of each mechanism that are responsible for the discrepancies with other mechanisms. The key question remaining is to determine what effect the differences in the mechanisms have on predicted organic control requirements. This aspect is the subject of Part III.

In Part III the effect of several parameters (initial VOC composition, dilution, post 8-A.M. emissions, base case ozone, entrainment of VOC and ozone from aloft, initial HONO and VOC/NO_x ratio) on the amount of VOC control needed to achieve the ozone NAAQS of 0.12 ppm is studied. In Section 2 we describe the standard set of initial conditions we will employ and how the input parameters were changed for the sensitivity study. Section 3 contains a discussion of the results obtained and in Section 4 we attempt to explain some of the key sensitivity results using counter-species analysis. Section 5 summarizes the key findings of this study.

2. CHEMICAL MECHANISMS AND INPUT PARAMETERS

The goal of this study is to determine the effect of the choice of chemical reaction mechanism and of input parameters on the predicted organic (VOC) control requirements needed to meet the NAAQS for ozone. Specifically, we investigate how VOC control requirements obtained with six different mechanisms are influenced by such parameters as initial VOC composition, dilution, emissions, base case ozone, entrainment of VOC and ozone from aloft, initial HONO and VOC/NO_x ratio. From the information obtained in this study, we can determine to which parameters predicted VOC control requirements are most sensitive.

As noted in the Introduction, the basis of our approach is to use the EKMA method to generate ozone isopleths as a function of initial VOC and NO_x concentrations. The ozone isopleths are then used to calculate the VOC control needed to reduce the maximum ozone concentration from some present day (or base case) value to 0.12 ppm assuming no NO_x control and a specified VOC/NO_x ratio. In the EKMA procedure the chemical reaction mechanism is integrated with initial conditions representing the VOC/NO_x mixture typical of early morning conditions. The integration includes the effects of dilution, fresh emissions of VOC and NO_x from sources, and entrainment of species from aloft as the air parcel is diluted. Once the isopleths have been produced, the point corresponding to current (base case) conditions is found as that point on the ozone isopleth for the maximum 1-hr. average ozone concentration achieved in the region for which the $[VOC]_o/[NO_x]_o$ ratio is that of the air measured in the central area of the city over the period 6 A.M. to 9 A.M. on the day of the maximum ozone. Figure 1 shows a set of ozone isopleths calculated with one of the chemical mechanisms we will study. A point is shown on the 0.40 ppm isopleth at a $[VOC]_o/[NO_x]_o$ ratio of 10. The horizontal

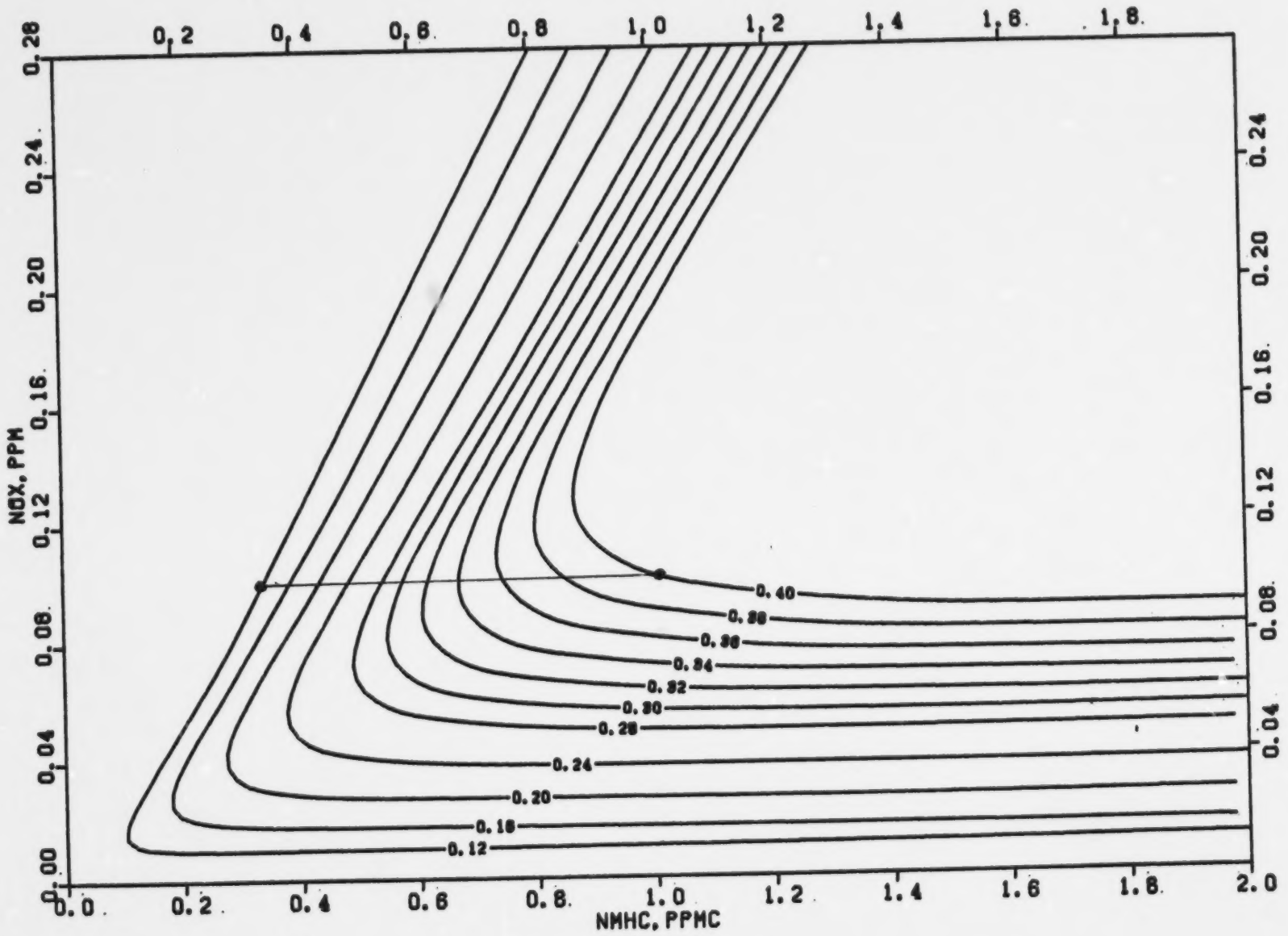

Figure 1. Typical Plot of Ozone Isopleths

line drawn from the point on the 0.40 ppm isopleth to the 0.12 ppm isopleth (the NAAQS for ozone) indicates that in order to reduce the maximum ozone from 0.40 to 0.12 ppm, without reducing the NO_x level, the initial VOC concentration must be reduced from 1.01 ppmC to 0.34 ppmC, that is by 66.3%. If VOC reduction is accompanied by NO_x increase or decrease, then one follows a line to the 0.12 ppm isopleth different from the horizontal line shown in Figure 1. Our study will be based on generating an ozone isopleth plot for each chemical reaction mechanism for each set of input parameters studied. Then the percent VOC reduction, or control, needed to go from a base case ozone point (the base case ozone concentration) at a given $[VOC]_o/[NO_x]_o$ ratio to the 0.12 ppm isopleth with no NO_x control will be calculated. These percent VOC controls will then be extensively compared.

The FORTRAN program ISOPLETH, a modified version of OZIPP, is used in this study. The FORTRAN program OZIPP, supplied by the EPA, uses the Dodge mechanism in the EKMA method to generate ozone isopleths. This program has been modified so that any chemical mechanism can be used. In the modified program, called ISOPLETH, the subroutines that integrate the rate equations have been replaced by a revised version of CHEMK (Whitten and Hogo, 1980). CHEMK is a FORTRAN program that integrates rate equations for any chemical reaction mechanism specified by the user (McRae, 1983). This program allows for variable photolysis rates. Two data files are needed to run ISOPLETH. The first of these has the same format as the data file needed to run OZIPP. Because the original integration routines have been replaced, only the options TITL, ALRE, ACCU, DILU, PLAC, ISOP and PLOT are available. The data supplied in this file are used to determine how the isopleths are constructed. The second data file is very similar to that needed to run CHEMK. Gipson (1985) repeated some of our calculations using OZIPM-2 and obtained the same VOC control requirements. The full computer

program is available from the authors.

2.1 Input Parameters for Standard Ozone Isopleth Diagrams

The input parameters needed to generate the standard ozone isopleths diagram are, for any mechanism:

(1) initial VOC concentration, $[VOC]_o$

(2) initial NO_x concentration, $[NO_x]_o$

(3) time of simulation

(4) NO_2 photolysis rate *

(5) temperature

(6) concentrations of "background species", H_2O and CO

(7) dilution rate

(8) concentrations of species entrained from aloft

(9) input concentrations corresponding to fresh emissions

(10) initial concentrations of other species required by the mechanism, e.g. HONO

Although ISOPLETH automatically picks the initial VOC and NO_x concentrations to generate an array of points in the plane, the user must indicate the compositon of the initial VOC mixture, NO/NO_2 ratio and the initial concentration of the other species required in a mechanism. The initial VOC composition will be varied and will be discussed shortly. The $[NO]_o/[NO_2]_o$ ratio used in this study is 6. The initial H_2O concentration is 15500 ppm and that of CO is 1.90 ppm. Each simulation will be run at a constant temperature of 298 K for ten hours, a time sufficient for the maximum ozone concentration to be reached in most cases. The NO_2 photolysis profile used corresponds to that for 8:00 A.M. - 6:00 P.M. on a clear September day in Los Angeles. (Table 1, Figure 2)

* The photolysis rates of the other species are usually determined from that for NO_2.

Table 1. NO_2 Photolysis Rate Profile

Time (minutes)	NO_2 Photolysis Rate (min^{-1})
0	0.30
60	0.39
120	0.44
180	0.46
240	0.47
300	0.46
360	0.41
420	0.34
480	0.24
540	0.11
600	0.02

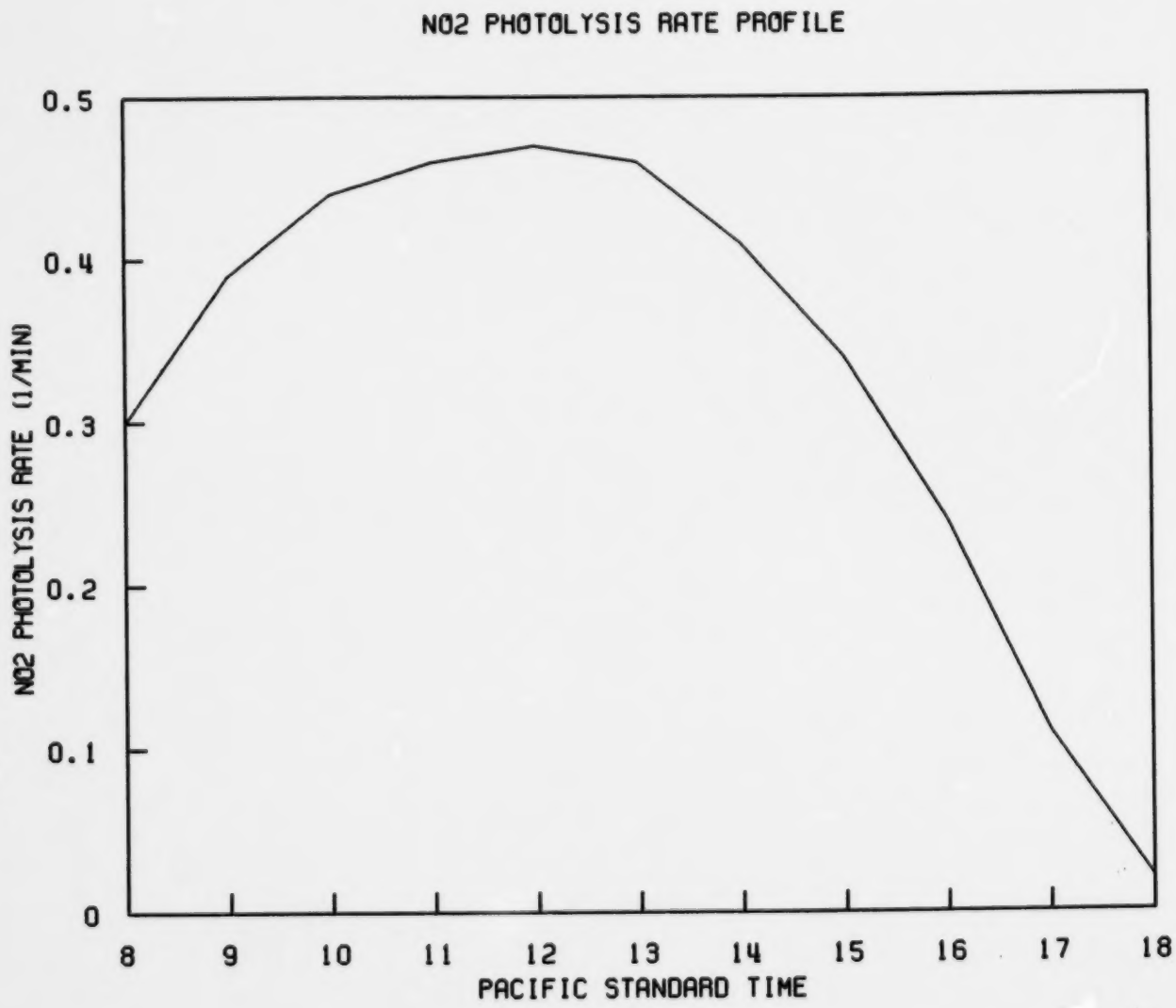
NO2 PHOTOLYSIS RATE PROFILE
NO2 PHOTOLYSIS RATE (1/MIN)
0.5
0.4
0.3
0.2
0.1
0
8
9
10
11
12
13
14
15
16
17
18
PACIFIC STANDARD TIME

Figure 2

As mentioned previously, we will study the effect of VOC composition, dilution, emissions, base case ozone, entrainment of VOC and ozone from aloft, initial HONO and the $[VOC]_o/[NO_x]_o$ ratio on the amount of VOC control needed to achieve the ozone standard.

2.2 Chemical Mechanisms

The chemical reaction mechaisms to be studied are those described and analyzed in Parts I and II:

Carbon Bond Mechanism (Killus and Whitten, 1982), referred to as CBM

Caltech Mechanism (McRae and Seinfeld, 1983), referred to as CIT

Demerjian Mechanism (Demerjian, 1982), referred to as DEM

Dodge Mechanism (Dodge, 1977), referred to as Dodge

Environmental Research and Technology Mechanism (Atkinson et al., 1982), referred to as ERT

Lawrence Livermore Laboratory Mechanism (Penner and Walton, 1982), referred to as PW

Each of the chemical reaction mechanisms uses a different scheme for splitting the initial VOC mixture into its lumped species (McRae et al., 1983). The Dodge mechanism is a surrogate mechanism, the CBM mechanism is a lumped structure mechanism and the others are lumped molecule mechanisms. When the Dodge mechanism is used, the initial VOC mixture is represented by a mixture of butane, propene, formaldehyde and acetaldehyde. The CBM mechanism breaks each species in the initial VOC mixture into its carbon components, which are then the lumped species used in this mechanism. The CIT, DEM, ERT and PW mechanisms group the components of the initial VOC mixture into lumped species. For example, in this approach all the alkanes in the initial VOC mixture are lumped into one or more species. When the PW mechanism is used, the concentration of the lumped

species is weighted according to the reactivity of the components of which it is comprised. The method for implementing these mechanisms is described in detail in Part I (McRae et al.) and will not be repeated here.

2.3 Initial VOC Composition

Two basic VOC mixtures will be used to study the effect of initial VOC composition on control predictions. These two VOC mixtures are given in Table 2. VOC mixture 1 will be taken as the standard organic mixture. It represents early morning pollutant levels in Los Angeles and was also used in Part II of this study. VOC mixture 2 is richer in aldehydes than mixture 1 and contains a lower percentage of alkanes and thus represents a more reactive surrogate.

The chemical mechanisms require that the initial organic mixture be apportioned into several lumped species. One can define a splitting factor for each species in each mechanism such that, when multiplied by the splitting factor, the initial VOC concentration in ppmC becomes the initial species concentration in ppm inputted into the mechanism. The splitting factors for each of the mechanisms for initial VOC mixtures 1 and 2 are listed in Table 3.

Because in earlier studies the initial aldehyde content has been shown to have a large effect on control predictions, we will study the effect of aldehydes specifically using the two additional initial VOC mixtures given in Table 4. Each of these two VOC mixtures has the same ratio of alkanes to olefins to aromatics as VOC mixture 1. The concentration of aldehydes, however, in these mixtures varies from 1.0 to 9.5 percent carbon. The splitting factors for the two mixtures are given in Table 5.

2.4 $[VOC]_o/[NO_x]_o$ Ratio

To study the effect of the other parameters on VOC control needed to reduce the maximum ozone concentration, a base case $[VOC]_o/[NO_x]_o$ ratio of 10 will be specified. $[VOC]_o/[NO_x]_o$ ratios of 6, 10 and 20 will be used to study the effect of

Table 2. Composition of Initial VOC Mixtures

Organic	Percent of carbon by volume VOC Mixture 1		VOC Mixture 2	
propane	2.4		1.7	
n-butane	30.4		21.4	
2,3-dimethylbutane	26.4		18.6	
ethene	4.0		5.6	
propene	1.8		2.5	
tr-2-butene	4.8		6.8	
toluene	5.6		6.6	
m-xylene	16.0		18.8	
formaldehyde	1.8		3.8	
acetaldehyde	2.0	4.4	4.2	9.2
propionaldehyde	0.6		1.2	
acetone	4.2		8.8	

Table 3. Splitting Factors[a] for Initial VOC Mixtures 1 and 2

Carbon Bond Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
ETH	2.0×10^{-2}	2.82×10^{-2}
OLE	6.0×10^{-3}	8.46×10^{-3}
ARO	2.8×10^{-2}	3.29×10^{-2}
PAR	7.0×10^{-1}	5.95×10^{-1}
CARB	6.8×10^{-2}	1.26×10^{-1}

Caltech Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
C_2H_4	2.0×10^{-2}	2.82×10^{-2}
HCHO	1.8×10^{-2}	3.76×10^{-2}
ARO	2.8×10^{-2}	3.29×10^{-2}
ALK	1.28×10^{-1}	9.02×10^{-2}
RCHO	1.2×10^{-2}	2.50×10^{-2}
OLE	1.8×10^{-3}	2.54×10^{-2}

Demerjian Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
HC1 (alkene)	3.8×10^{-2}	5.36×10^{-2}
HC2 (alkane)	1.42×10^{-1}	1.20×10^{-1}
HC3 (aldehyde)	3.0×10^{-2}	6.26×10^{-2}
HC4 (aromatic)	2.8×10^{-2}	3.29×10^{-2}

Dodge Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
PROP	8.33×10^{-2}	
BUT	1.875×10^{-1}	
HCH	2.0×10^{-2}	
ALD	1.5×10^{-2}	

Table 3. Splitting Factors[a] for Initial VOC Mixtures 1 and 2 (Continued)

ERT Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
ACL	1.0×10^{-2}	2.09×10^{-2}
PROP	8.0×10^{-3}	5.64×10^{-3}
ACT	1.4×10^{-2}	2.93×10^{-2}
ALK	1.2×10^{-1}	8.46×10^{-2}
ETH	2.0×10^{-2}	2.82×10^{-2}
RCH	2.0×10^{-3}	4.13×10^{-3}
PPEN	6.0×10^{-3}	8.46×10^{-3}
BTEN	1.2×10^{-2}	1.69×10^{-2}
XYL	2.0×10^{-2}	2.35×10^{-2}
TOL	8.0×10^{-3}	9.40×10^{-3}
HCH	1.8×10^{-2}	3.76×10^{-2}

PW Mechanism

Species	Splitting Factor[a] VOC Mixture 1	VOC Mixture 2
HC1 (alkene)	4.49×10^{-2}	6.32×10^{-2}
HC2 (alkane)	1.89×10^{-1}	1.33×10^{-1}
HC3 (aromatic)	8.00×10^{-2}	9.40×10^{-2}
HC4 (aldehyde)	2.95×10^{-2}	6.16×10^{-2}

[a]Splitting factor x initial VOC concentration (ppmC by volume) = species concentration (ppmV).

Table 4. Composition of Initial VOC Mixtures 3 and 4

Organic	Percent of Carbon by Volume VOC Mixture 3		VOC Mixture 4	
propane	2.57		2.14	
n-butane	32.6		27.1	
2,3-dimethylbutane	28.3		23.5	
ethene	4.29		3.56	
propene	1.93		1.60	
tr-2-butene	5.15		4.28	
toluene	6.01		4.99	
m-xylene	17.2		14.3	
formaldehyde	0.409	1.0%	3.89	9.5%
acetaldehyde	0.455		4.32	
propionaldehyde	0.136		1.30	
acetone	0.955		9.07	

Table 5. Splitting Factors[a] for Initial VOC Mixtures 3 and 4

Carbon Bond Mechanism

Species	Splitting Factors[a] VOC Mixture 3	VOC Mixture 4
ETH	2.15×10^{-2}	1.78×10^{-2}
OLE	6.44×10^{-3}	5.35×10^{-3}
ARO	3.01×10^{-2}	2.49×10^{-2}
PAR	7.15×10^{-1}	6.77×10^{-1}
CARB	3.58×10^{-2}	1.16×10^{-1}

Caltech Mechanism

Species	Splitting Factors[a] VOC Mixture 3	VOC Mixture 4
C_2H_4	2.15×10^{-2}	1.78×10^{-2}
HCHO	4.09×10^{-3}	3.89×10^{-2}
ARO	3.01×10^{-2}	2.49×10^{-2}
ALK	1.37×10^{-1}	1.14×10^{-1}
RCHO	2.73×10^{-3}	2.59×10^{-2}
OLE	1.93×10^{-2}	1.61×10^{-2}

Demerjian Mechanism

Species	Splitting Factors[a] VOC Mixture 3	VOC Mixture 4
HC1 (alkene)	4.08×10^{-2}	3.39×10^{-2}
HC2 (alkane)	1.40×10^{-1}	1.44×10^{-1}
HC3 (aldehyde)	6.82×10^{-3}	6.48×10^{-2}
HC4 (aromatic)	3.01×10^{-2}	2.49×10^{-2}

ERT Mechanism

Species	Splitting Factors[a] VOC Mixture 3	VOC Mixture 4
ACL	2.27×10^{-3}	2.16×10^{-2}
PROP	8.58×10^{-3}	7.13×10^{-3}
ACT	3.18×10^{-3}	3.02×10^{-2}
ALK	1.29×10^{-1}	1.07×10^{-1}

Table 5. Splitting Factors[a] for Initial VOC Mixtures 3 and 4 (Continued)

ERT Mechanism (continued)

Species	Splitting Factors[a]	
	VOC Mixture 3	VOC Mixture 4
ETH	2.15×10^{-2}	1.78×10^{-2}
RCH	4.55×10^{-4}	4.32×10^{-3}
PPEN	6.44×10^{-3}	5.35×10^{-3}
BTEN	1.29×10^{-2}	1.07×10^{-2}
XYL	2.15×10^{-2}	1.78×10^{-2}
TOL	8.58×10^{-3}	7.13×10^{-3}
HCH	4.09×10^{-3}	3.89×10^{-2}

Penner and Walton Mechanism

Species	Splitting Factors[a]	
	VOC Mixture 3	VOC Mixture 4
HC1 (alkene)	4.82×10^{-2}	4.00×10^{-2}
HC2 (alkane)	2.03×10^{-1}	1.68×10^{-1}
HC3 (aromatic)	8.58×10^{-2}	7.12×10^{-2}
HC4 (aldehyde)	6.70×10^{-3}	6.37×10^{-2}

[a]Splitting factor x initial VOC concentration (ppmC by volume) = species concentration (ppmV).

$[VOC]_o/[NO_x]_o$ ratio on control prediction using initial VOC mixtures 1 and 2 and either no entrainment, ozone entrainment or VOC entrainment.

2.5 Base Case Ozone

The percent VOC control needed to reduce the maximum ozone concentration to 0.12 ppm depends on the base case ozone concentration. We will study the effect of changing the base case ozone concentration from 0.40 to 0.24 using both VOC mixtures 1 and 2.

2.6 Dilution

The dilution rate that we will study corresponds to an increase in mixing height from 250 to 1235 meters over a period of about 7.5 hours (Gipson, 1983b). This profile (Figure 3) has been used by the U.S. E.P.A. Office of Air Quality and Planning and Standards (OAQPS) and is typical of a fairly well ventilated region such as Washington D.C. (Whitten and Hogo, 1978). Unless specified otherwise, when dilution occurs, the air entrained will be pollutant free. Dilution will be studied with VOC mixtures 1 and 2, assuming a base case ozone concentration of 0.24 ppm.

2.7 Emissions

The effect of post-8 A.M. emissions will be studied using two different scenarios, in each of which 15 percent of the initial concentration of VOC and NO_x will be added each hour. The initial VOC composition will be that of VOC mixture 1 for the two scenarios. In the first scenario the composition of VOC emissions will be that of VOC mix 1 and in the second scenario the composition of VOC emissions will be that of VOC mix 2. Thus, in the second scenario the post-8 A.M. emissions are greater in reactivity than the initial mix. This is a reasonable scenario because the 6-9 A.M. mix contains some carry-over (surface transported VOC's) that would be less reactive than the fresh unreacted emissions.

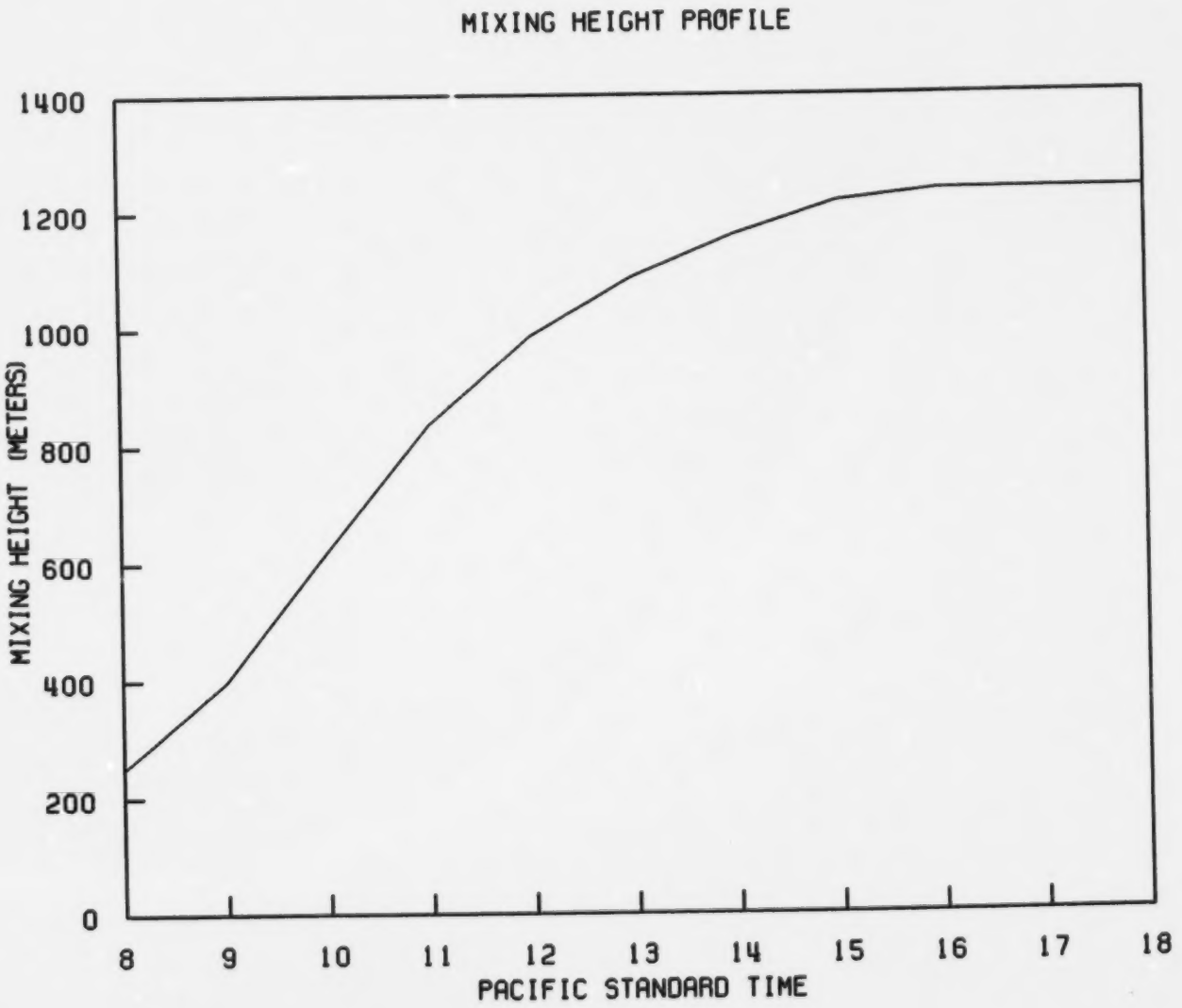
MIXING HEIGHT PROFILE
MIXING HEIGHT (METERS)
1400
1200
1000
800
600
400
200
0
8
9
10
11
12
13
14
15
16
17
18
PACIFIC STANDARD TIME

Figure 3

2.8 Entrainment of VOC and Ozone from Aloft

The entrainment of VOC and ozone from aloft will be studied assuming an increase in mixing height from 250 to 1235 meters. To include entrainment from aloft a chemical reaction with no reactants and the entrained species as the product is added to the mechanism. The rate constant for the reaction is equal to the product of the dilution rate and the species concentration aloft. To study VOC entrainment we will assume 0.05 ppmC VOC aloft, an estimate suggested by Gipson (1983b). Because we expect the composition of the entrained VOC mixture to affect control predictions, four different entrained VOC mixes will be studied. Neither ozone nor NO_x is included in the entrained mixes. The first three of these mixtures represent low, mid and high background pollution levels. The aldehyde contents of these mixtures are 9, 26 and 17 percent, respectively. (Killus and Whitten, 1983) The remainder of each of the three mixes contains the same proportions of the organics as VOC mix 1 allowing for aging of the entrained air mass. The fourth mixture contains no carbonyls. For the low background mix we assume that everything except propane, n-butane and acetone has reacted. This is a well-aged air mass. Twenty percent of the n-butane and acetone is assumed to have been depleted. For the mid background mix all of the propene and tr-2-butene have been depleted due to reaction with ozone. Ten percent of the ethene, twenty percent of the butane and acetone, sixty percent of the toluene and 80 percent of the 2,3-dimethylbutane and m-xylene have also reacted. For the high background mix we assume little aging of the air mass has occurred and only propene and tr-2-butene have been depleted. In the "no carbonyls" mixture we assume the same composition as the mid-range mixture except that there are no aldehydes. This case enables us to estimate how much of the effect of VOC aloft is due solely to the assumed aldehyde content. The VOC compositions for these four cases are shown in Table 6. Control predictions will

Table 6. Composition of VOC Mixtures Entrained from Aloft

Organic	Percent of Carbon			
	Mid	Low	High	No Carbonyls
propane	4.0	7.2	2.2	5.4
n-butane	40.6	73.5	28.5	54.8
2,3-dimethylbutane	8.8	-	24.6	12.0
ethene	5.9	-	3.7	7.9
propene	-	-	-	-
tr-2-butene	-	-	-	-
toluene	3.7	-	5.2	5.0
m-xylene	5.3	-	14.9	7.2
formaldehyde	21	7	14	-
acetaldehyde	5	2	3	-
propionaldehyde	-	-	-	-
acetone	5.7	10.3	3.9	7.7

be calculated using a $[VOC]_o/[NO_x]_o$ ratio of 10 and a base case ozone concentration of 0.24 ppm. With the mid background mix, the effects of reducing base case ozone to 0.18 ppm and starting with VOC mix 2 on control predictions will also be studied using $[VOC]_o/[NO_x]_o$ ratios of 6, 10 and 20. The effect of VOC entrainment will also be studied with the mid background mix assuming emissions and an initial VOC/NO_x ratio of 10. The effect of ozone entrainment will be studied assuming base case ozone concentrations of 0.24 and 0.18 ppm and $[VOC]_o/[NO_x]_o$ ratios of 20, 10 and 6. The concentration of ozone aloft is assumed to be 0.08 ppm.

2.9 Initial HONO

Because HONO photolyzes to form OH radicals, the initial mixture is more reactive if HONO is assumed to be present initially (Harris et. al., 1982). We will study the effect of the presence of HONO in the initial mixture with VOC mixtures 1 and 2.

3. SENSITIVITY OF VOC CONTROL PREDICTIONS TO INPUT PARAMETERS AND CHEMICAL MECHANISM

In this section our object is to determine how each of the input parameters influences control predictions and how these predictions vary among the mechanisms. It will be seen that not all mechanisms respond the same to changes in selected parameters. The predictions of some mechanisms are quite sensitive to certain parameters; the predictions obtained with other mechanisms are largely insensitive to these same parameters.

3.1 Initial VOC Composition

The first parameter investigated in this study is the composition of the initial VOC mix. VOC control predictions needed to reduce the maximum ozone concentration from 0.40 ppm to 0.12 ppm (VOC/NO_x=10)† for both mixture 1 and the more reactive mixture 2 are shown in Table 7. The percent control is defined as

$$Red = \frac{VOC_o - VOC_f}{VOC_o} \times 100$$

VOC_o=VOC concentration at base case ozone concentration

VOC_f=VOC concentration at 0.12 ppm ozone assuming no NO_x control.

The percentage difference Δ between the control predictions at the two initial VOC mixes is also calculated,‡

$$\Delta = \frac{Red(A) - Red(B)}{Red(B)} \times 100$$

† The ratio VOC/NO_x will refer to the initial concentrations, previously written as $[VOC]_o/[NO_x]_o$.

‡ Δ should only be used as a guide when comparing control predictions because it is highly dependent on Red(B).

Table 7. Effect of Initial VOC Mixture on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.40 to 0.12 ppm[a]

Mechanism	VOC Mixture 1			VOC Mixture 2			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]
CBM	1.01	0.34	66.3	1.01	0.25	75.2	13.4
CIT	1.10	0.45	59.1	1.00	0.32	68.0	15.1
DEM	1.13	0.52	54.0	0.97	0.35	63.9	18.3
ERT	1.55	0.78	49.7	1.54	0.56	63.6	28.0
PW	1.19	0.48	59.7	1.09	0.33	69.7	16.8

[a] $VOC/NO_x = 10$
no dilution
no entrainment from aloft
no NO_x control
no emissions ; base case ozone = 0.40 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $$Red = \frac{VOC_o - VOC_f}{VOC_o} \times 100$$

[e] $$\Delta = \frac{Red(VOC2) - Red(VOC1)}{Red(VOC1)} \times 100$$

Red(X)= percent control needed assuming initial conditions X

Conclusions to be drawn from Table 7:

(1) The more reactive the mix, the more VOC control that is needed to achieve the ozone standard.

(2) Choice of chemical mechanism has a large effect on control predictions. For example, when VOC mix 1 is assumed, the ERT mechanism predicts 49.7 percent VOC control whereas the CBM mechanism predicts 66.3 percent control.

(3) The choice of chemical mechanism has a large impact on the sensitivity of the predictions to a change in VOC composition. The ERT mechanism is most sensitive to a change in the overall reactivity of the VOC mix (Δ = 28.0%). The CBM is the least sensitive (Δ = 13.4%). Thus, if you are exercising the ERT mechanism, it is more important that you accurately describe the 6-9 A.M. composition of the VOC mix than if you are performing control stategy calculations with the CBM.

Thus far we have looked at changing the overall reactivity of the VOC mix. That is, VOC mix 2 has a higher proportion of olefins, aromatics and aldehydes than does VOC mix 1. Next we will study the effect of changing only the aldehyde content of the mix, that is VOC mixtures 3 and 4. The results are shown in Table 8.

Conclusions to be drawn from Table 8:

(1) Predicted control is very sensitive to the aldehyde content of the initial VOC mix.

(2) When aldehydes are increased from 1 to 4.4%, the PW mechanism shows the greatest sensitivity, the CBM shows the least. But when aldehydes are further increased to 9.5%, the ERT mechanism shows the greatest sensitivity, and the DEM shows the least.

We have shown the sensitivity of the mechanisms to an overall increase in VOC reactivity and the sensitivity to an increase only in the aldehyde content of the VOC mix. Next we will show how the various mechanisms respond to an increase in the reactivity of a VOC mix by increasing only the proportion of olefins and aromatics

Table 8. Effect of Aldehyde Content on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.40 to 0.12 ppm

Mechanism	VOC Mixture 3(ALD=1%)			VOC Mixture 1(ALD=4.4%)				VOC Mixture 4(ALD=9.5%)			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_c[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]	VOC_c[b]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
CBM	1.05	0.40	61.9	1.01	0.34	66.3	6.6	0.98	0.29	70.4	6.2
CIT	1.23	0.60	51.2	1.10	0.45	59.1	13.4	1.04	0.38	63.5	7.4
DEM	1.17	0.59	49.6	1.13	0.52	54.0	8.1	1.09	0.47	56.9	5.4
ERT	1.95	1.11	43.1	1.55	0.78	49.7	13.3	1.50	0.63	58.0	16.7
PW	1.27	0.63	50.4	1.19	0.48	59.7	15.6	1.17	0.41	65.0	8.9

[a] VOC/NO_x = 10; no dilution; no entrainment from aloft; no NO_x control; no emissions; base case ozone = 0.40 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(VOC1) - Red(VOC3)}{Red(VOC1)} \times 100$

[f] $\frac{Red(VOC4) - Red(VOC1)}{Red(VOC1)} \times 100$

relative to the alkanes by comparing the predictions obtained with VOC mix 4 to those obtained with mixture 2. These two mixtures have almost the same aldehyde content. (9.5% for VOC4 compared to 9.2% for VOC2) The comparison is shown in Table 9.

Conclusions to be drawn from Table 9 :

If you compare Δ(%) shown in Table 9 to the Δ(%) shown in Table 8, you can see that on the whole most mechanisms respond about equally to a change in the olefin and aromatic content of the mix as they do to a change in the aldehyde content with some exceptions. The ERT mechanism, however, is much more sensitive to a change in aldehyde content than to a change in hydrocarbon content. (Compare 13.3% and 16.7% in Table 8 to 9.7% in Table 9.) The DEM mechanism shows the greatest sensitivity of all the mechanisms to a change in hydrocarbon composition (12.3%) but it showed about the least sensitivity of the mechanisms to a change in aldehyde content (8.1% and 5.4%).

3.2 VOC/NO_x Ratio

When determining the sensitivity of control predictions to a change in VOC composition of the initial mix the VOC/NO_x ratio was assumed to be 10. The choice of the VOC/NO_x ratio has a large effect on control predictions as shown in Table 10 where VOC/NO_x ratios of 6 and 20 are presented.

Conclusions to be drawn from Table 10 :

(1) The mechanisms agree most closely with one another at high VOC/NO_x ratios.

(2) In every case the CBM mechanism showed the least sensitivity to a change in VOC/NO_x ratio.

(3) In three of the four cases, the ERT mechanism showed the greatest sensitivity to a change in VOC/NO_x ratio. For VOC mixture 1, however, the PW mechanism showed the greatest sensitivity when the VOC/NO_x ratio was increased from 6 to 10.

(4) In every case, the more reactive the mixture, the less the effect of the VOC/NO_x ratio on predicted control stategies. But regardless of the VOC composition, predictions are extremely sensitive to the VOC/NO_x ratio.

The effect of changing the composition of the VOC mixture at the three VOC/NO_x

Table 9. Effect of Olefin and Aromatic Content on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.40 to 0.12 ppm[a]

Mechanism	VOC Mixture 4			VOC Mixture 2			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]
CBM	0.98	0.29	70.4	1.01	0.25	75.2	6.8
CIT	1.04	0.38	63.5	1.00	0.32	68.0	7.1
DEM	1.09	0.47	56.9	0.97	0.35	63.9	12.3
ERT	1.50	0.63	58.0	1.54	0.56	63.6	9.7
PW	1.17	0.41	65.0	1.09	0.33	69.7	7.2

[a] VOC/NO_x = 10; no dilution; no entrainment from aloft; no NO_x control no emissions; base case ozone = 0.40 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(VOC2) - Red(VOC4)}{Red(VOC4)} \times 100$

Table 10. Effect of VOC/NO_x Ratio on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.40 to 0.12 ppm[a]

Mechanism	VOC/NO_x = 6			VOC/NO_x = 10				VOC/NO_x = 20			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
VOC Mixture 1											
CBM	0.89	0.47	47.2	1.01	0.34	66.3	28.8	1.66	0.29	82.5	24.4
CIT	1.69	1.00	40.8	1.10	0.45	59.1	31.0	1.75	0.39	77.7	31.5
DEM	1.79	1.16	35.2	1.13	0.52	54.0	34.8	1.58	0.40	74.7	38.3
Dodge	1.71	0.94	45.0	1.80	0.62	65.6	31.4	3.29	0.58	82.4	25.6
ERT	4.19	2.83	32.5	1.55	0.78	49.7	34.6	2.87	0.71	75.3	51.5
PW	1.47	0.96	34.7	1.19	0.48	59.7	51.8	1.77	0.37	79.1	32.5
VOC Mixture 2											
CBM	0.73	0.29	60.3	1.01	0.25	75.2	24.7	1.95	0.24	87.7	16.6
CIT	0.96	0.47	51.0	1.00	0.32	68.0	33.3	1.96	0.32	83.7	23.1
DEM	0.95	0.50	47.4	0.97	0.35	63.9	34.8	1.63	0.30	81.6	27.7
ERT	1.62	0.90	44.4	1.54	0.56	63.6	43.2	3.38	0.63	82.2	29.2
PW	0.89	0.43	51.7	1.09	0.33	69.7	34.8	1.78	0.27	84.8	21.7

[a] No dilution; no entrainment from aloft, no NO_x control; no emissions; base case ozone = 0.40 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(10) - Red(6)}{Red(10)} \times 100$

[f] $\frac{Red(20) - Red(10)}{Red(10)} \times 100$

ratios can be determined by comparing the % reduction for VOC1 to the % reduction for VOC2. The Δ's obtained in this comparison are shown in Table 11.

Conclusions to be drawn from Table 11 :

(1) The sensitivity of predictions to a change in the composition of the VOC mix is greatest at low VOC/NO_x ratios. At high ratios, the predictions are little altered by a change in the reactivity of the VOC mix. It is not as important, therefore, to characterize the composition of VOC emissions in urban areas with a high VOC/NO_x ratio as it is in urban areas with a low VOC/NO_x ratio.

(2) At low ratios, the PW mechanism is the most sensitive to changes in VOC composition; the CIT mechanism is the least sensitive.

(3) At medium VOC/NO_x ratios, the ERT mechanism is the most sensitive and the CBM, the least.

(4) At high ratios, the ERT and DEM mechanisms exhibit the greatest sensitivity; CBM shows the least.

3.3 Base Case Ozone

Thus far, all the sensitivity studies have shown the effect of changes when ozone is reduced from 0.40 to 0.12 ppm. A base case ozone value of 0.40, however, is higher than most urban areas experience. (Even in Los Angeles, peak ozone in recent years generally does not exceed 0.35 ppm.) The effect of lowering base case ozone from 0.40 to 0.24 ppm is shown in Table 12.

Conclusions to be drawn Table 12 :

(1) The highest control is pred ed for the highest starting ozone concentration.

(2) The mechanisms show a greater spread in predicted control requirements for low base case ozone.

(3) When VOC1 is assumed the DEM mechanism is most sensitive and the CBM mechanism least sensitive to changes in base case ozone.

(4) When VOC2 is assumed the CIT mechanism is most sensitive and the PW mechanism is least sensitive to changes in base case ozone.

Table 11. Effect of Changing VOC Composition at Different VOC/NO_x Ratios[a]

Mechanism	VOC/NO_x=6 $\Delta(\%)$[b]	VOC/NO_x=10 $\Delta(\%)$[b]	VOC/NO_x=20 $\Delta(\%)$[b]
CBM	27.8	13.4	6.3
CIT	25.0	15.1	7.7
DEM	34.7	18.3	9.2
ERT	26.8	28.0	9.2
PW	49.0	16.8	7.2

[a] No dilution; no entrainment from aloft; no NO_x control, no emissions, base case ozone = 0.40 ppm

[b] $$\Delta(\%) = \frac{\text{Red(VOC2)-Red(VOC1)}}{\text{Red(VOC1)}} \times 100$$

Table 12. Effect of Base Case Ozone[a] on Predicted Control Strategies Under Conditions of No Dilution

Mechanism	Base Case O_3=0.40 ppm			Base Case O_3=0.24 ppm			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[e]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
VOC Mixture 1							
CBM	1.01	0.34	66.3	0.43	0.17	60.5	8.7
CIT	1.10	0.45	59.1	0.42	0.22	47.6	19.5
DEM	1.13	0.52	54.0	0.44	0.26	40.9	24.3
Dodge	1.80	0.62	65.6	0.80	0.35	56.3	14.2
ERT	1.55	0.78	49.7	0.71	0.39	45.1	9.3
PW	1.19	0.48	59.7	0.48	0.22	54.2	9.2
VOC Mixture 2							
CBM	1.01	0.25	75.2	0.42	0.12	71.4	5.1
CIT	1.00	0.32	68.0	0.36	0.15	58.3	14.3
DEM	0.97	0.35	63.9	0.36	0.16	55.6	13.0
ERT	1.54	0.56	63.6	0.65	0.27	58.5	8.0
PW	1.09	0.33	69.7	0.44	0.14	68.2	2.2

[a] VOC/NO_x = 10; no dilution; no entrainment; no NO_x control; no emissions

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[f] $\frac{Red(O_3=0.40) - Red(O_3=0.24)}{Red(O_3=0.40)} \times 100$

The effect of changing VOC composition as a function of base case ozone can be determined by calculating the Δ's for the % reduction columns. These Δ's are shown in Table 13.

Conclusions to be drawn from Table 13

The effects of changes in VOC composition are more pronounced the lower the base case ozone. Therefore, it is not as critical to accurately represent the composition of an urban mix in areas experiencing high ozone as it is in areas experiencing low ozone.

3.4 Dilution

Control predictions assuming an increase in mixing height from 250 to 1235 meters using the OAPQS characteristic curve and a base case ozone concentration of 0.24 ppm, using initial VOC mixtures 1 and 2 are given in Table 14

Conclusions to be drawn from Table 14

(1) The mechanisms show a greater spread in predicted control requirements when dilution is considered.

(2) The ERT mechanism shows more sensitivity to a change in the dilution for the less reactive mix (VOC1). All other mechanisms show about the same sensitivity for both mixtures.

(3) The ERT mechanism is most sensitive to dilution corresponding to an increase in mixing height from 250 to 1235 meters when VOC1 is assumed and the DEM mechanism is most sensitive when VOC2 is assumed. When VOC1 is assumed the Dodge mechanism is least sensitive whereas when VOC2 is assumed the CBM mechanism is least sensitive.

The effect of dilution on changing VOC composition can be seen by looking down the columns. The Δ's calculated for each dilution rate when VOC mixture 2 is substituted for VOC mixture 1 are shown in Table 15.

Conclusions to be drawn from Table 15

The percent changes (Δ) ranged from 18.0% to 35.9% when no dilution was included in the simulations to a range of 18.8% to 35.4% for an increase in

Table 13. Effect of Changing VOC Composition at Different Base Case Ozone Values[a]

Mechanism	Base Case O_3 = 0.40 ppm $\Delta(\%)$[b]	Base Case O_3 = 0.24 ppm $\Delta(\%)$[b]
CBM	13.4	18.0
CIT	15.1	22.5
DEM	18.3	35.9
ERT	28.0	29.7
PW	16.8	25.8

[a] VOC/NO_x=10, no dilution, no NO_x control, no entrainment from aloft, no emissions.

[b] $\Delta(\%) = \frac{Red(VOC2)-Red(VOC1)}{Red(VOC1)} \times 100$

Table 14. Effect of Dilution on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.24 to 0.12 ppm[a]

Mechanism	No dilution			dilution[f]			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]
VOC Mixture 1							
CBM	0.43	0.17	60.5	2.86	1.26	55.9	7.6
CIT	0.42	0.22	47.6	2.83	1.60	43.5	8.6
DEM	0.44	0.26	40.9	2.83	1.83	35.3	13.7
Dodge	0.80	0.35	56.3	4.75	2.05	56.8	-0.8
ERT	0.71	0.39	45.1	4.10	2.58	37.1	17.7
PW	0.48	0.22	54.2	3.11	1.60	48.6	10.3
VOC Mixture 2							
CBM	0.42	0.12	71.4	2.83	0.95	66.4	7.0
CIT	0.36	0.15	58.3	2.68	1.25	53.4	8.4
DEM	0.36	0.16	55.6	2.45	1.28	47.8	14.0
ERT	0.65	0.27	58.5	4.10	1.95	52.4	10.4
PW	0.44	0.14	68.2	2.78	1.07	61.5	9.8

[a] VOC/NO_x = 10; no entrainment from aloft; no NO_x control; base case ozone = 0.24 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(No) - Red(dilution)}{Red(No)}$

[f] increase in mixing height from 250 to 1235m using the OAQPS characteristic curve

Table 15. Effect of Changing VOC Composition at Different Dilution Rates[a]

Mechanism	No dilution Δ(%)[b]	dilution[c] Δ(%)
CBM	18.0	18.8
CIT	22.5	22.8
DEM	35.9	35.4
ERT	29.7	29.2
PW	25.8	26.5

[a] $NMHC/NO_x$ = 10; no entrainment from aloft; no NO_x control; base case ozone = 0.24 ppm

[b] $\Delta(\%) = \frac{Red(VOC2)-Red(VOC1)}{Red(VOC1)} \times 100$

[c] increase in mixing height from 250 to 1235m using the OAQPS characteristic curve.

mixing height from 250 to 1235 meters. Dilution does not change significantly the effect of VOC composition on control predictions.

3.5 Emissions

Next we examine the effect of post-8 A.M. emissions on control predictions needed to meet the NAAQS standard for ozone. In Table 16 control predictions assuming no emissions, emission scenario 1 and emission scenario 2 are compared. Recall that emission scenario 1 assumes that the composition of VOC emissions is the same as the initial VOC mix whereas scenario 2 assumes that the VOC emissions mix is more reactive than the initial VOC mix.

Conclusions to be drawn from Table 16

(1) Although as expected, the VOC concentrations corresponding to base case ozone and 0.12 ppm ozone are less when emissions are added, the percent control actually decreases for all mechanisms except the Dodge, when emission scenario 1 is assumed. When emissions are added a given percent reduction represents a larger reduction in total VOC in the atmosphere than when no emissions are added.

(2) When emission scenario 2 is assumed, the Δ's range between -6.7 and 3.1. Because the reactivity of the emissions is higher than that of the initial VOC mix, more control is needed than when emission scenario 1 is used.

(3) The PW mechanism is most sensitive and the DEM mechanism least sensitive to the addition of emissions.

In Table 17 the effect of varying the VOC/NO_x ratio of the initial VOC and NO_x mixture on control prediction is shown. By comparing Tables 10 and 17 the effect of emissions on the sensitivity of the VOC/NO_x ratio is seen.

Conclusions to be drawn from Table 17

(1) As with the case when no emissions are present, control predictions increase with increasing VOC/NO_x ratio.

(2) The Δ's are larger when emissions are included. For example, when the VOC/NO_x ratio is increased from 10 to 20 the CBM mechanism yields a 31.9% change when emissions are included and a 24.4% change without emissions.

Table 16. Effect of Emissions on VOC Control Needed to Reduce Maximum O_3 from 0.40 to 0.12 ppm[a]

	No Emissions			Emissions[b] (VOC1 composition)				Emissions[c] (VOC2 composition)			
Mechanism	VOC_o[d]	VOC_f[e]	Red(%)[f]	VOC_o[d]	VOC_f[e]	Red(%)[f]	Δ(%)[g]	VOC_o[d]	VOC_f[e]	Red(%)[f]	Δ(%)[h]
CBM	1.01	0.34	66.3	0.54	0.22	59.3	-10.6	0.53	0.19	64.2	-3.2
CIT	1.10	0.45	59.1	0.63	0.31	50.8	-14.0	0.58	0.25	56.9	-3.7
DEM	1.13	0.52	54.0	0.58	0.30	48.3	-10.6	0.53	0.24	54.7	+1.3
ERT	1.55	0.78	49.7	1.05	0.60	42.9	-13.7	0.85	0.44	48.2	+3.1
PW	1.19	0.48	59.7	0.62	0.31	50.0	-16.2	0.61	0.27	55.7	-6.7
Dodge	1.80	0.62	65.6	1.27	0.42	66.9	2.0				

[a] VOC/NO_x = 10; no dilution; no entrainment from aloft; no NO_x control; base case ozone = 0.40 ppm

[b] 15% of initial NO_x and VOC emitted each hour; VOC emissions same composition as VOC1.

[c] 15% of initial NO_x and VOC emitted each hour; VOC emissions same composition as VOC2.

[d] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm

[e] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[f] $$\frac{VOC_o - VOC_f}{VOC_o} \times 100$$

[g] $$\Delta(\%) = \frac{\text{Red(VOC1)} - \text{Red(no emissions)}}{\text{Red (no emissions)}} \times 100$$

[h] $$\Delta(\%) = \frac{\text{Red(VOC2)} - \text{Red(no emissions)}}{\text{Red(no emissions)}} \times 100$$

Table 17. Effect of Adding Emissions with VOC Composition Different from the 6-9 AM VOC Composition at Different VOC/NO_x ratios[a]

Mechanism	VOC/NO_x = 6			VOC/NO_x = 10				VOC/NO_x = 20			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
			(1)			(2)				(3)	
CBM	0.54	0.31	42.6	0.53	0.19	64.2	33.6	1.18	0.18	84.7	31.9
CIT	1.12	0.70	37.5	0.58	0.25	56.9	34.1	0.87	0.20	77.0	35.0
DEM	0.74	0.48	35.1	0.53	0.24	54.7	35.8	0.87	0.20	77.0	40.8
ERT	3.14	2.30	26.8	0.85	0.44	48.2	44.4	1.65	0.40	75.8	57.3
PW	0.94	0.64	31.9	0.61	0.27	55.7	42.7	1.00	0.22	78.0	40.0

[a] No dilution; no entrainment aloft; no NO_x control; VOC mixture 1; base case ozone = 0.40 ppm

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\Delta(\%) = \frac{Red(2) - Red(1)}{Red(2)} \times 100$

[f] $\Delta(\%) = \frac{Red(3) - Red(2)}{Red(2)} \times 100$

Therefore, it is more important to know the true VOC/NO_x ratio when emissions are present.

3.6 Entrainment of VOC and Ozone from Aloft

We next study the effect on control predictions of entrainment of VOC and ozone from aloft. Table 18 compares control predictions assuming no entrainment and entrained VOC mixtures having the low, mid and high background pollution levels given in Table 6. For these simulations we assume 0.05 ppmC VOC aloft and a base case ozone concentration of 0.24 ppm.

Conclusions to be drawn from Table 18

(1) Control predictions change between 4 and 21 percent when entrainment is added.

(2) Between 3.9 (Dodge) and 6.2% (CIT, DEM and ERT) more control is needed when the low background pollution mixture is entrained than without entrainment.

(3) Between 5.3 (Dodge) and 20.7% (DEM) more control is needed when the mid background pollution mixture is entrained.

(4) Between 6.2 (Dodge) and 16.4% (DEM) more control is needed when the high background pollution mixture is entrained.

(5) When either the DEM, CIT or ERT mechanism is used it is more important to know the composition and concentration of the entrained mixture than when the other mechanisms are used.

In Table 19 the effect of entraining the "mid" background pollution mix from aloft is shown using initial VOC/NO_x ratios of 6 and 20 is shown.

Conclusions to be drawn from Table 19

(1) When either the CBM, Dodge or PW mechanism is used the lower the initial VOC/NO_x ratio, the larger the effect of VOC entrainment from aloft on control predictions. For the CIT and ERT mechanisms the effect of VOC entrainment is largest at an initial VOC/NO_x ratio of 10 and smallest at an initial VOC/NO_x ratio of 20. When the DEM mechanism is used, the effect is largest at an initial ratio of 10 and smallest at an initial ratio of 6.

Table 18. Effect of VOC Entrainment from Aloft[a]

Mechanism	No Entrainment VOC_o[b]	VOC_f[c]	Red(%)[d]	"Low" Entrainment VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]
CBM	2.86	1.26	55.9	2.80	1.14	59.3	6.1
CIT	2.83	1.60	43.5	2.73	1.47	46.2	6.2
DEM	2.83	1.83	35.3	2.80	1.75	37.5	6.2
Dodge	4.75	2.05	56.8	4.58	1.88	59.0	3.9
ERT	4.10	2.58	37.1	3.96	2.40	39.4	6.2
PW	3.11	1.60	48.6	2.98	1.46	51.0	4.9

	"Mid" Entrainment			Δ(%)[f]	"High" Entrainment			Δ(%)[g]
CBM	2.80	1.03	63.2	13.1	2.83	1.07	62.2	11.3
CIT	2.70	1.34	50.4	15.9	2.71	1.39	48.7	12.0
DEM	2.72	1.56	42.6	20.7	2.75	1.62	41.1	16.4
Dodge	4.55	1.83	59.8	5.3	4.58	1.82	60.3	6.2
ERT	3.90	2.23	42.8	15.4	3.95	2.30	41.8	12.7
PW	2.97	1.33	55.2	13.6	2.98	1.37	54.0	11.1

[a] VOC/NO_x = 10; base case ozone = 0.24; no emissions; no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m using the OAQPS characteristic curve; 0.05 ppmC (by volume) VOC entrained from aloft.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(Low) - Red(No)}{Red(No)} \times 100$

[f] $\frac{Red(Mid) - Red(No)}{Red(No)} \times 100$

[g] $\frac{Red(High) - Red(No)}{Red(No)} \times 100$

Table 19. Effect of VOC ("Mid Range" Composition) Entrainment from Aloft at Different VOC/NO_x Ratios[a]

Mechanism	No Entrainment VOC_o[b]	No Entrainment VOC_f[c]	No Entrainment Red(%)[d]	"Mid" Entrainment VOC_o[b]	"Mid" Entrainment VOC_f[c]	"Mid" Entrainment Red(%)[d]	Δ(%)[e]
VOC/NO_x = 6							
CBM	2.46	1.59	35.4	2.26	1.31	42.0	18.6
CIT	4.35	3.08	29.2	3.71	2.53	31.8	8.9
DEM	5.13	3.87	24.6	4.38	3.21	26.7	8.5
Dodge	4.32	2.75	36.3	4.02	2.39	40.5	11.6
ERT	10.2	7.86	22.9	8.94	6.67	25.4	10.9
PW	3.91	2.98	23.8	3.03	2.13	29.7	24.8
VOC/NO_x = 20							
CBM	4.45	1.06	76.2	4.40	0.87	80.2	5.2
CIT	4.28	1.35	68.5	4.20	1.10	83.8	7.7
DEM	3.10	1.25	59.7	3.04	1.05	65.5	9.7
Dodge	5.36	1.58	70.5	5.36	1.40	73.9	4.8
ERT	6.47	2.15	66.8	6.35	1.85	70.9	6.1
PW	4.37	1.23	71.9	4.50	1.05	76.7	6.7

[a] base case ozone = 0.24; no emissions, no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m using OAQPS characteristic curve; 0.05 ppmC (by volume) VOC entrained from aloft

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC Concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(Mid) - Red(No)}{Red(No)} \times 100$

(2) At an initial VOC/NO_x ratio of 6 the PW mechanism is most sensitive to the entrainment of VOC from aloft; the DEM mechanism is least sensitive.

(3) At an initial VOC/NO_x ratio of 20 the DEM mechanism is most sensitive to the entrainment of VOC from aloft; the Dodge mechanism is least sensitive.

In Table 20 the effect of entrainment of the mid background VOC mix is shown using a base case ozone concentration of 0.18 ppm and initial VOC/NO_x ratios of 6, 10 and 20.

Conclusions to be drawn from Table 20

(1) As is the case when a base case ozone concentration of 0.24 ppm is assumed, for either the CBM, Dodge or PW mechanism the lower the initial VOC/NO_x ratio the larger the effect of VOC entrainment from aloft. For the other mechanisms the effect of VOC entrainment is largest at an initial VOC/NO_x ratio of 10 and smallest at an initial ratio of 20.

(2) At an initial VOC/NO_x of 6 the PW mechanism is most sensitve to the entrainment of VOC from aloft. The ERT mechanism is least sensitive.

(3) At initial VOC/NO_x ratios of 10 and 20 the DEM mechanism is most sensitive to VOC entrainment from aloft. The Dodge mechanism is least sensitive.

In Table 21 the effect of reducing base case ozone from 0.24 to 0.18 ppm is shown using the mid background pollution mix.

Conclusions to be drawn from Table 21

Between 8.5% (PW) and 22.8% (DEM) more control is needed when the base case ozone is 0.24 ppm than when base case ozone is 0.18 ppm. Therefore, when the DEM mechanism is used, it is more important to determine the present day maximum ozone concentration. Recall that the DEM mechanism is also most sensitive to changes in base case ozone when entrainment and dilution were not included in the simulations (Table 12).

In Table 22 the effect of carbonyls in the entrained VOC mix is shown assuming initial VOC/NO_x ratios of 6, 10 and 20. The "mid"reactive mixture has 26% carbonyls (as carbon) versus a mixture containing no carbonyls. (see Table 6).

Conclusions to be drawn from Table 22

Table 20. Effect of VOC ("Mid" Range" Composition) Entrainment from Aloft for Base Case Ozone = 0.18 ppm[a]

Mechanism	No Entrainment VOC_o[b]	No Entrainment VOC_f[c]	No Entrainment Red(%)[d]	"Mid" Entrainment VOC_o[b]	"Mid" Entrainment VOC_f[c]	"Mid" Entrainment Red(%)[d]	Δ(%)[e]
VOC/NO_x = 6							
CBM	1.60	1.20	25.0	1.40	0.91	35.0	40.0
CIT	2.79	2.23	20.1	2.19	1.69	22.8	13.4
DEM	3.42	2.91	14.9	2.89	2.40	17.0	14.1
Dodge	2.81	2.07	26.3	2.54	1.73	31.9	21.3
ERT	6.36	5.36	15.7	5.02	4.16	17.1	8.9
PW	2.21	1.82	17.6	1.73	1.30	24.9	41.5
VOC/NO_x = 10							
CBM	1.84	0.95	48.4	1.80	0.78	56.7	17.1
CIT	1.83	1.24	32.2	1.65	0.95	42.4	31.7
DEM	1.82	1.38	24.2	1.67	1.12	32.9	36.0
Dodge	3.09	1.67	46.0	2.96	1.44	51.4	11.7
ERT	2.60	1.84	29.2	2.46	1.52	38.2	30.8
PW	1.92	1.12	41.7	1.88	0.93	50.5	21.1
VOC/NO_x = 20							
CBM	3.00	0.87	71.0	2.96	0.71	76.0	7.0
CIT	2.80	1.06	62.1	2.76	0.85	69.2	11.4
DEM	2.20	1.05	52.3	2.18	0.89	59.2	13.2
Dodge	3.67	1.60	56.4	3.61	1.44	60.1	6.6
ERT	4.46	1.62	63.7	4.20	1.30	69.0	8.3
PW	2.77	0.97	65.0	2.60	0.75	71.2	9.5

[a] Base case ozone = 0.18; no emissions, no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m using the OAQPS characteristic curve; 0.05 ppmC (by volume) VOC entrained from aloft.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.18 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(Mid) - Red(No)}{Red(No)} \times 100$

Table 21. Effect of Base Case Ozone Concentration with Entrainment of VOC ("Mid Range" Composition) from Aloft[a]

Mechanism	Base Case Ozone = 0.24			Base Case Ozone = 0.18			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[e]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
CBM	2.80	1.03	63.2	1.80	0.78	56.7	10.3
CIT	2.70	1.34	50.4	1.65	0.95	42.4	15.9
DEM	2.72	1.56	42.6	1.67	1.12	32.9	22.8
Dodge	4.55	1.83	59.8	2.96	1.44	51.4	14.0
ERT	3.90	2.23	42.8	2.46	1.52	38.2	10.7
PW	2.97	1.33	55.2	1.88	0.93	50.5	8.5

[a] VOC/NO_x = 10; no emissions; no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m assuming the OAQPS characteristic curve; 0.05 ppmC (by volume) VOC entrained from aloft.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] VOC concentration (ppmC by volume) when maximum concentration is 0.18 ppm.

[f] $\frac{Red(0.24) - Red(0.18)}{Red(0.24)} \times 100$

Table 22. Effect of Carbonyls on VOC Entrainment from Aloft[a]

Mechanism	"Mid" Entrainment VOC_o[b]	"Mid" Entrainment VOC_f[c]	"Mid" Entrainment Red(%)[d]	"No Carbonyls" Entrainment VOC_o[b]	"No Carbonyls" Entrainment VOC_f[c]	"No Carbonyls" Entrainment Red(%)[d]	Δ(%)[e]
VOC/NO_x = 6							
CBM	2.26	1.31	42.0	2.30	1.45	37.0	11.9
CIT	3.71	2.53	31.8	4.20	2.90	31.0	2.5
DEM	4.38	3.21	26.7	4.56	3.40	25.4	4.9
Dodge	4.02	2.39	40.5	4.16	2.55	38.7	4.4
ERT	8.94	6.67	25.4	10.2	7.80	23.5	7.5
PW	3.03	2.13	29.7	3.42	2.50	26.9	9.4
VOC/NO_x = 10							
CBM	2.80	1.03	63.2	2.80	1.15	58.9	6.8
CIT	2.70	1.34	50.4	2.76	1.50	45.7	9.3
DEM	2.72	1.56	42.6	2.80	1.70	39.3	7.7
Dodge	4.55	1.83	59.8	4.65	1.91	58.9	1.5
ERT	3.90	2.23	42.8	3.99	2.44	38.8	9.3
PW	2.97	1.33	55.2	2.99	1.49	50.2	9.1
VOC/NO_x = 20							
CBM	4.40	0.87	80.2	4.38	0.95	78.3	2.4
CIT	4.20	1.10	73.8	4.14	1.25	69.8	5.4
DEM	3.04	1.05	65.5	3.00	1.12	62.7	4.3
Dodge	5.36	1.40	73.9	5.50	1.48	73.1	1.1
ERT	6.35	1.85	70.9	6.50	2.09	67.8	4.4
PW	4.50	1.05	76.7	4.50	1.18	73.8	3.8

[a] Base Case Ozone = 0.24; no emissions, no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m using the OAQPS curve; 0.05 ppmC (by volume) VOC entrained from aloft.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(Mid) - Red(NO)}{Red(Mid)} \times 100$

(1) Assuming an initial VOC/NO_x ratio of 6 the CBM mechanism is most sensitive ($\Delta = 11.9\%$) to increasing the percent carbonyls in the entrained mixture from 0% to 26%. The CIT mechanism ($\Delta = 2.5\%$) is least sensitive.

(2) Assuming an initial VOC/NO_x ratio of 10 the CIT and ERT mechanisms are most sensitive ($\Delta = 9.3\%$) and the Dodge mechanism ($\Delta = 1.5\%$) is least sensitive to a change in carbonyl content of the entrained mixture.

(3) Assuming an initial VOC/NO_x ratio of 20 the CIT mechanism is most sensitive ($\Delta = 5.4\%$) and the Dodge mechanism ($\Delta = 1.1\%$) is least sensitive to a change in carbonyl content of the entrained mixture.

(4) Using an initial VOC/NO_x ratio of 10, the ERT mechanism is most sensitve to a change in carbonyl content (Table 8) as well as being one of the most sensitive mechanisms to carbonyl content in the entrained VOC mixture as expected. Also note that the CIT mechanism is one of the most sensitive mechanisms to both VOC entrainment (Table 18) and carbonyl content of the entrained mixture.

Table 23 shows the effect of initial VOC composition when the "mid" background pollution mix is entrained from aloft assuming initial VOC/NO_x ratios of 6, 10 and 20.

Conclusions to be drawn from Table 23

(1) More control is needed when VOC mixture 2 is used instead of VOC mixture 1 as the initial VOC mix. (Δ's are between 25.5% and 53.9% at an initial VOC/NO_x ratio of 6, between 13.4% and 32.5% for an initial VOC/NO_x ratio of 10 and between 4.5% and 8.7% for an initial ratio of 20.)

(2) For all the mechanisms except the ERT mechanism the effect of the composition of the initial VOC mixture is less when entrainment of VOC from aloft is assumed (Table 15).

(3) Consistent with previous results more control is needed at higher VOC/NO_x ratios (Table 10) and the effect of changing the initial VOC composition is largest at low VOC/NO_x ratios (Table 11).

The effect of VOC entrainment from aloft assuming emissions and a dilution rate corresponding to an increase in mixing height from 250 to 1235 meters is shown in Table 24. The composition of the VOC emissions is assumed to be the same as VOC mixture 1.

Table 23. Effect of Initial VOC Composition with Entrainment of VOC ("Mid Range" Composition) from Aloft[a]

Mechanism	VOC1 VOC_o[b]	VOC1 VOC_f[c]	VOC1 Red(%)[d]	VOC2 VOC_o[b]	VOC2 VOC_f[c]	VOC2 Red(%)[d]	Δ(%)[e]
VOC/NO_x = 6							
CBM	2.26	1.31	42.0	1.92	0.89	53.6	27.6
CIT	3.71	2.53	31.8	2.18	1.31	39.9	25.5
DEM	4.38	3.21	26.7	2.34	1.53	34.6	29.6
ERT	8.94	6.67	25.4	3.42	2.23	34.8	37.0
PW	3.03	2.13	29.7	2.23	1.21	45.7	53.9
VOC/NO_x = 10							
CBM	2.80	1.03	63.2	2.83	0.80	71.7	13.4
CIT	2.70	1.34	50.4	2.69	1.06	60.6	20.2
DEM	2.72	1.56	42.6	2.37	1.10	49.4	16.0
ERT	3.90	2.23	42.8	3.97	1.72	56.7	32.5
PW	2.97	1.33	55.2	2.78	0.96	65.5	18.7
VOC/NO_x = 20							
CBM	4.40	0.87	80.2	3.89	0.63	83.8	4.5
CIT	4.20	1.10	73.8	3.60	0.78	78.3	6.1
DEM	3.04	1.05	65.5	2.30	0.70	69.6	6.3
ERT	6.35	1.85	70.9	5.60	1.28	77.1	8.7
PW	4.50	1.05	76.7	3.91	0.73	81.3	6.0

[a] Base case ozone = 0.24; no emissions, no NO_x control; increase in mixing height from 250 to 1235m using the OAQPS curve; 0.05 ppmC (by volume) entrained VOC from aloft.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(VOC2) - Red(VOC1)}{Red(VOC1)} \times 100$

Table 24. Effect of Entrainment of VOC("Mid Range") Composition from Aloft with Emissions[a]

Mechanism	No Entrainment			"Mid" Entrainment			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]
CBM	0.77	0.48	37.7	0.72	0.39	45.8	21.5
CIT	1.11	0.77	30.6	0.91	0.58	36.3	18.6
DEM	0.83	0.61	26.5	0.72	0.48	33.3	25.7
Dodge	1.63	0.89	45.4	1.62	0.79	51.2	12.8
ERT	2.19	1.67	23.7	1.75	1.28	26.9	13.5
PW	1.51	0.40	73.5	1.48	0.32	78.4	6.7

[a] Base case ozone = 0.24; 15% of initial NO_x and VOC emitted each hour; VOC emissions same composition as VOC1; no NO_x control; VOC mix 1; increase in mixing height from 250 to 1235m using the OAQPS characteristic curve; entrained VOC from aloft = 0.05 ppmC (by volume)

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(Mid) - Red(No)}{Red(No)} \times 100$

Conclusions to be drawn from Table 24

(1) Control requirements increase between 6.7% (PW) and 25.7% (DEM) when entrainment is included.

(2) The CBM, DEM and Dodge mechanisms are more sensitive to VOC entrainment when emissions are included in the simulation. The PW mechanism is more sensitive to VOC entrainment without emissions. The CIT and ERT mechanisms show about the same sensitivity to VOC entrainment whether or not emissions are included.

The effect of entraining 0.08 ppm ozone using a dilution rate corresponding to an increase in mixing height from 250 to 1235 meters is shown in Table 25 assuming base case ozone of 0.24 and 0.18 ppm.

Conclusions to be drawn from Table 25

(1) The DEM mechanism is most sensitive to ozone entrainment (Δ=40.2%). The CBM mechanism is least sensitive (Δ =8.1%). This finding is consistent with the conclusion that the DEM mechanism is also most sensitive to base case ozone concentration.

(2) The Dodge mechanism is most sensitive to decreasing base case ozone from 0.24 to 0.18 ppm (Δ=30.9%). The PW mechanism is least sensitive (Δ=1.1%).

Table 26 shows the effect of VOC/NO_x ratio on control predictions assuming 0.08 ppm ozone aloft and base case ozone of 0.24 ppm.

Conclusions to be drawn from Table 26

(1) Control predictions increase with increasing VOC/NO_x ratio. This is consistent with previous findings (Table 10).

(2) As we found when studying the effect of VOC/NO_x without entrainment and dilution and with emissions, control predictions are very sensitive to this parameter. Therefore, it is necessary to determine as accurately as possible this ratio, regardless of the other input parameters.

3.7 Initial HONO

The last parameter investigated in this study was initial HONO. The results obtained when initial HONO was included in the simulations using initial mixtures

Table 25. Effect of Entrainment of 0.08 ppm O_3 on VOC Control for Two Base Case Ozone Values[a]

Mechanism	Base Case O_3 = 0.24 ppm No Entrainment			Base Case O_3 = 0.24 ppm O_3(aloft) = 0.08 ppm				Base Case O_3 = 0.18 ppm O_3(aloft) = 0.08 ppm			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]	VOC_o[f]	VOC_f[c]	Red(%)[d]	Δ(%)[g]
			(1)			(2)				(3)	
CBM	2.86	1.26	55.9	2.22	0.88	60.4	8.1	1.28	0.60	53.1	12.1
CIT	2.83	1.60	43.5	2.13	1.07	49.8	14.5	1.22	0.74	39.3	21.1
DEM	2.83	1.83	35.3	2.22	1.12	49.5	40.2	1.26	0.71	43.7	11.7
Dodge	4.75	2.05	56.8	3.66	1.35	63.1	11.1	2.11	1.19	43.6	30.9
ERT	4.10	2.58	37.1	3.27	1.79	45.3	22.1	1.84	1.08	41.3	8.8
PW	3.11	1.60	48.6	2.53	1.09	56.9	17.1	1.44	0.63	56.3	1.1

[a] VOC/NO_x = 10; VOC mixture 1: no emissions; no NO_x control; increase in mixing height from 250 to 1235m assuming the OAQPS curve.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $$\frac{VOC_o - VOC_f}{VOC_o} \times 100$$

[e] $$\Delta(\%) = \frac{Red(2) - Red(1)}{Red(1)} \times 100$$

[f] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.18 ppm.

[g] $$\Delta(\%) = \frac{Red(2) - Red(3)}{Red(2)} \times 100$$

Table 26. Effect of VOC/NO_x Ratio with the Entrainment of 0.08 ppm Ozone from Aloft[a]

Mechanism	VOC/NO_x = 6			VOC/NO_x = 10				VOC/NO_x = 20			
	VOC_o[b]	VOC_f[c]	Red(%)[d]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[e]	VOC_o[b]	VOC_f[c]	Red(%)[d]	Δ(%)[f]
			(1)			(2)				(3)	
CBM	2.01	1.21	39.8	2.22	0.88	60.4	34.1	3.53	0.76	78.5	30.0
CIT	3.38	2.20	34.9	2.13	1.07	49.8	29.9	3.20	0.85	73.4	47.4
DEM	3.45	2.40	30.4	2.22	1.12	49.5	38.6	2.48	0.70	71.8	45.1
Dodge	3.33	1.86	44.1	3.66	1.35	63.1	30.1	4.66	0.99	78.8	24.9
ERT	8.22	6.10	25.8	3.27	1.79	45.3	43.0	5.03	1.43	71.6	58.1
PW	2.93	2.05	30.0	2.53	1.09	56.9	47.3	3.53	0.78	77.9	36.9

[a] VOC mixture 1; base case ozone = 0.24; no emissions ; no NO_x control; increase in mixing height from 250 to 1235m assuming the OAQPS characteristic curve.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm.

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm.

[d] $\frac{VOC_o - VOC_f}{VOC_o} \times 100$

[e] $\frac{Red(2) - Red(1)}{Red(2)} \times 100$

[f] $\frac{Red(3) - Red(2)}{Red(2)} \times 100$

1 and 2 are shown in Table 27.

Conclusions to be drawn from Table 27

Predictions obtained with the ERT mechanism are most sensitive to initial HONO; predictions obtained with the PW mechanism are least sensitive.

The effect of changing composition of the VOC mixture when HONO is included in the simulations can be determined by comparing the Red(%) for VOC1 and VOC2. The results are show in Table 28.

Conclusions to be drawn from Table 28

The ERT mechanism shows the greatest sensitivity to changes in VOC composition when HONO is included; CBM mechanism shows the least sensitivity. This is also the case when HONO is not included in the calculations. All mechanisms, except for the PW mechanism show less sensitivity to VOC compositional changes when HONO is included in the simulations.

3.8 Summary of Results

Results presented in this chapter are summarized in Table 29. For most of the parameters investigated, we have indicated the mechanism that exhibited the most and least sensitivity when that parameter was varied and the range of Δ (%) obtained.

Conclusions to be drawn from Table 29

(1) There is no one mechanism that is most or least sensitive to all of the variables studied.

(2) The ERT mechanism is most sensitive to the most number of parameters (9 out of 19).

(3) The CBM mechanism is least sensitive to the most number of parameters (9 out of 19).

(4) Because the effects of input parameters have not been tested against experimental data, it is not possible to pick the best mechanism by examining the data presented in this table. Rather this table should be use to emphasize the necessity to look at several chemical mechanisms and to characterize the input

Table 27. Effect of Initial HONO on VOC Control Needed to Reduce Maximum Ozone Concentration from 0.40 to 0.12 ppm[a]

Mechanism	no initial HONO			initial HONO = 5.0% initial NO_x			
	VOC_o[b]	VOC_f[c]	Red(%)	VOC_o[b]	VOC_f[c]	Red(%)	Δ(%)[d]
VOC Mixture 1							
CBM	1.01	0.34	66.3	0.97	0.29	70.1	5.7
CIT	1.10	0.45	59.1	1.06	0.41	61.3	3.7
DEM	1.13	0.52	54.0	1.09	0.48	56.0	3.7
Dodge	1.80	0.62	65.6	1.74	0.58	66.7	1.7
ERT	1.55	0.78	49.7	1.43	0.64	55.2	11.1
PW	1.19	0.48	59.7	1.19	0.48	59.7	0
VOC Mixture 2							
CBM	1.01	0.25	75.2	0.98	0.23	76.5	1.7
CIT	1.00	0.32	68.0	0.97	0.30	69.1	1.6
DEM	0.97	0.35	63.9	0.95	0.33	65.3	2.2
ERT	1.54	0.56	63.6	1.47	0.49	66.7	4.9
PW	1.09	0.33	69.7	1.10	0.33	70.0	0.4

[a] VOC/NO_x = 10; no dilution; no entrainment from aloft; no NO_x control; base case ozone = 0.40 ppm; no emissions

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm

[d] $\Delta(\%) = \frac{\text{Red(HONO)} - \text{Red(no HONO)}}{\text{Red(no HONO)}} \times 100$

Table 28. Effect of Changing VOC Composition in the Absence and Presence of HONO[a]

Mechanism	No initial HONO $\Delta(\%)^b$	$(HONO)_i = 0.05\ (NO_x)_i$ $\Delta(\%)^b$
CBM	13.4	9.1
CIT	15.1	12.7
DEM	18.3	16.6
ERT	28.0	20.8
PW	16.8	17.3

[a] VOC/NO_x = 10; no dilution; no entrainment from aloft, no NO_x control; base case ozone = 0.40 ppm; no emissions

[b] $\Delta(\%) = \frac{Red(VOC2)-Red(VOC1)}{Red(VOC1)} \times 100$

Table 29. Summary of Results[a]

Variable	Most. Sen.	Least Sen.	Δ(%)
Overall reactivity of $(VOC)_i$	ERT	CBM	13-28
Proportion of OLE + ARO in $(VOC)_i$	DEM	CBM	7-12
Proportion of ALD in $(VOC)_i$	ERT	DEM	5-17
Overall reactivity of $(VOC)_i$, $VOC/NO_x = 6$	PW	CIT	25-49
Overall reactivity of $(VOC)_i$, $VOC/NO_x = 20$	DEM/ERT	CBM	6-9
VOC/NO_x (lower from 10 to 6)	PW	CBM	29-52
VOC/NO_x (raise from 10 to 20)	ERT	CBM	24-52
Dilution	PW	Dodge	0-20
Base-case O_3 (lower from 0.40 to 0.24 ppm)	DEM	CBM	9-24
Emissions (composition same as initial mix)	CIT	Dodge	-14-+2
Emissions (composition different than initial mix)	PW	DEM	-6.7-+1.3
Emissions (different composition, VOC/NO_x=6)	ERT	CBM	33-45
Emissions (different composition VOC/NO_x=10)	ERT	CBM	32-57
VOC aloft (low reactivity)dilution	CIT,DEM,ERT	Dodge	3.9-6.2
VOC aloft (mid reactivity) dilution	DEM	Dodge	5.3-20.7
VOC aloft (high reactivity) dilution	DEM	Dodge	6.2-16.4
VOC aloft (no carbonyls) dilution	CIT,ERT	Dodge	1.5-9.3
O_3 aloft, dilution, base case O_3 = 0.24 ppm	DEM	CBM	8.1-40.2
$[HONO]_i$	ERT	PW	0-11.1

[a]Unless noted otherwise, composition of initial VOC is VOC Mixture 1, VOC/NO_x = 10; no dilution, base case O_3 = 0.40 ppm.

parameters as carefully as possible before deciding what control requirements are needed.

Using the conditions assumed in this study, the parameters are ranked in order of decreasing sensitivity on control predictions.

(1) Initial VOC/NO_x ratio

(2) Ozone entrained from aloft

(3) Initial VOC composition

(4) Base case ozone, dilution and VOC entrained from aloft

(5) emissions and initial HONO

This ranking should be used only as a guideline since it depends on the conditions that we studied. For example, the effect of the initial VOC mixture on control predictions was calculated assuming a base case ozone concentration of 0.40 ppm whereas the effect of ozone entrained from aloft was calculated assuming a base case ozone concentration of 0.24 ppm. As noted before, the lower the base case ozone concentration, the larger the effect of an input parameter on control predictions.

3.9 Comparison of Results to Those of Previous Investigators

We can compare the results of this study with those of Carter, Dunker, Jeffries and Gipson (Carter et al., 1982; Dunker et al., 1984; Jeffries et al., 1981; Gipson, 1983a, 1983b,1985). Each of these studies used the EKMA method to predict the maximum ozone concentration. Carter et al. (1982) studied the effect of the VOC/NO_x ratio and the composition of the initial hydrocarbon mixture on VOC control using the Dodge and Carter mechanisms. As we have shown in this study the control predictions were found to be quite sensitive to the initial VOC/NO_x ratio. Removing aldehydes from the initial hydrocarbon mixture decreased control requirements by approximately 20 percent, consistent with our findings.

Dunker et al. (1984) studied the effect of choice of chemical mechanism on

control requirements needed to reduce the maximum ozone concentration from 0.30 to 0.12 ppm. They used the Dodge, CIT, CBM and ELSTAR mechanisms. Using the initial surrogate mixture of the Dodge mechanism as the initial VOC mixture, they predicted between 68 and 84 percent control for the different mechanisms assuming an initial VOC/NO_x ratio of 10. The six chemical reaction mechanisms that we studied yield control predictions similar to those of Dunker et al.

Jeffries et al. (1981) used the DEM, Dodge and CBM mechanisms to predict the effect on control requirements of the choice of chemical mechanism, ozone entrainment from aloft and composition of the initial VOC mixture. In this study each set of input parameters represented actual measurements taken during 1976. They found that choice of chemical mechanism and ratio of ozone entrainment to generated ozone had a large effect on control predictions. The effect of aldehyde concentration in the initial hydrocarbon mixture depended on the day being studied. We also found control predictions to be quite sensitive to ozone entrainment.

Gipson (1983a,b) studied the effect of VOC entrainment from aloft and the initial VOC composition using a newer version of the CBM mechanism and the effect of initial HONO and choice of chemical mechanism using the CBM and Dodge mechanisms. In agreement with the other studies, Gipson found that the composition of initial hydrocarbon mixture and choice of chemical mechanism have a large effect on control requirements. In agreement with our study, the effect of initial HONO on control predictions was found to be small. Gipson's study showed that VOC entrained from aloft has a large effect on control requirements. Assuming 0.04 ppmC aloft, Gipson found that the VOC control requirements increased to 59% from 38% (Δ=55%) when no VOC were entrained, at an initial VOC/NO_x ratio of 8, assuming 26% aldehydes in the entrained mix, emissions and a base case ozone concentration of 0.17 ppm. When Gipson computed control from the predicted ozone

peak (0.223 ppm with entrainment and 0.232 ppm without entrainment), the control level with entrainment was 58% and without entrainment was 46% (Δ=26%). With the same dilution rate, no emissions, a base case ozone concentration of 0.24 ppm, and assuming 0.05 ppmC aloft, we predict 35.4% control without entrainment and 42.0% control with entrainment (Δ=19%) at an initial VOC ratio of 6. Using an initial VOC/NO_x ratio of 10 predicted control is 55.9% without entrainment and 63.2% with entrainment (Δ =13%). With variable emissions and 0.08 ppm ozone entrained from aloft we find an increase in control from 35.6% to 45.2% (Δ =21%) at an initial VOC/NO_x of 10. Gipson (1985) also determined the effect of VOC entrainment from aloft on VOC control with and without emissions assuming an initial VOC/NO_x ratio of 10 and a base case ozone concentration of 0.24 ppm, using the same version of the CBM mechanism as used in this study. Without emissions and 0.04 ppm VOC entrained from aloft, control increased from 60% to 67% (Δ =12%) when no VOC were entrained. With emissions and 0.05 ppm ozone entrained from aloft, control predictions with VOC entrainment increased to 55% from 45% (Δ =22%) without VOC entrainment. Therefore, both studies show that for the carbon bond mechanism the sensitivity for VOC entrainment on control requirements is highly dependent on whether or not emissions are included in the simulations.

In summary, the results presented in this study are generally consistent with those of previous investigators who have studied the sensitivity of hydrocarbon reductions to choice of chemical mechanism and input parameters.

4. DISCUSSION OF RESULTS

The previous section contains a great deal of information concerning the sensitivity of VOC control predictions to input parameters and chemical mechanisms. We found that different mechanisms respond differently to changes in input parameters and that the mechanisms exhibiting the greatest and least sensitivity depend on what input parameter is being studied. The object of this section is to attempt to explain some of the key sensitivity results of the previous section. Specifically, we seek to explain the sensitivity, or lack thereof, of different mechanisms to certain input parameters on the basis of the essential chemical nature of the mechanism. In other words, we will attempt to answer the general question - Why is mechanism A more sensitive than mechanism B to a change in an input parameter? - for a number of the key cases of the previous section. Since the measure of a mechanism's performance on which we are focusing is its ozone predictions, the method employed in Part II based on determining the number of NO to NO_2 conversions attributable to each VOC class is applicable here. Thus, to assess the sensitivity of a mechanism to changes in input parameters, we will determine the NO to NO_2 conversions attributable to each VOC class and the total NO to NO_2 conversions under both pre- and post-control situations.

4.1 Initial VOC Compositions

In section 3.1 we found that, under the conditions studied, the ERT mchanism is most sensitive to a change in initial VOC composition, and the CBM mechanism is the least sensitive. The percent of NO to NO_2 conversions attributable to each VOC class is given in Table 30 for both mechanisms under pre- and post-control conditions using VOC mixtures 1 and 2. The most notable difference between the two mechanisms is that for the ERT mechanism the percent of NO to NO_2

Table 30. Percent of Total NO to NO_2 Conversions Due to Each Organic Class Using VOC Mixtures 1 and 2 for the CBM and ERT Mechanisms[a]

Organic class	VOC Mixture 1 pre-control[b]	VOC Mixture 1 post-control[c]	VOC Mixture 2 pre-control[b]	VOC Mixture 2 post-control[c]
ERT Mechanism				
Aromatics	22.9	28.0	23.2	27.3
Alkanes	39.8	29.6	24.4	17.8
Alkenes	28.0	29.9	35.6	34.2
Aldehydes	9.2	12.5	16.8	20.6
Total (ppb)	525.2	228.7	530.5	219.5
CBM Mechanism				
Aromatics	31.7	33.3	31.2	31.3
Alkanes	32.1	26.5	17.2	14.3
Alkenes	21.8	22.5	26.3	25.2
Aldehydes	14.4	17.7	25.4	29.1
Total (ppb)	468.8	169.0	489.0	164.0

[a] VOC/NO_x = 10; no dilution; no NO_x control; no entrainment from aloft; no emissions

[b] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.40 ppm (Table 7).

[c] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.12 ppm (Table 7).

conversions due to aromatics increases in post-control conditions over pre-control conditions, for example from 22.9% to 28.0% using VOC1, whereas for the CBM mechanism this percentage remains approximately constant (33.3% vs. 31.7%). The difference in percent NO to NO_2 conversions attributable to alkanes between pre- and post-control conditions is also larger for the ERT mechanism. Thus, we expect the ERT mechanism should be more sensitive to a change in initial VOC composition than the CBM mechanism.

Continuing our analysis, we seek to explain why the percentage of NO to NO_2 conversions attributable to aromatics and alkanes changes more for the ERT mechansism than for the CBM mechanism. In Part II of this study we found that the ERT mechanism predicts fewer NO to NO_2 conversions due to aromatics than the other mechanisms. This behavior was found to result from an assumption that 25% of the aromatic-OH-O_2 adduct is assumed to react with NO to yield nitrates. At higher VOC/NO_x ratios corresponding to pre-control conditions, this nitrate forming step is more influential than at the lower VOC/NO_x ratios characteristic of post-control conditions. The CBM mechanism predicts more NO to NO_2 conversions attributable to aromatics than the ERT mechanism because of the higher photolysis rate of methyl glyoxal used. The consumption of conjugated-γ-dicarbonyls is also faster in the CBM mechanism than in the ERT mechanism. Since both of these steps are independent of the VOC/NO_x ratio, the percent of NO to NO_2 conversions attributable to aromatics in the CBM mechanism is not expected to change appreciably between pre- and post-control conditions. This is, in fact, what is observed.

In Section 3.1 we also showed that the ERT mechanism is most sensitive to a change in aldehyde content and the CBM mechanism is least sensitive. Table 31 shows the percent of NO to NO_2 conversions attributable to each VOC class

Table 31. Percent of Total NO to NO_2 Conversions Due to Each Organic Class Using VOC Mixtures 1 and 4 for the CBM and ERT Mechanisms[a]

Organic class	VOC Mixture 1 pre-control[b]	VOC Mixture 1 post-control[c]	VOC Mixture 4 pre-control[b]	VOC Mixture 4 post-control[c]
ERT Mechanism				
Aromatics	22.9	28.0	19.3	24.6
Alkanes	39.8	29.6	36.4	25.3
Alkenes	28.0	29.9	24.4	24.9
Aldehydes	9.2	12.5	20.0	25.2
Total (ppb)	525.2	228.7	522.3	203.2
CBM Mechanism				
Aromatics	31.7	33.3	26.5	26.9
Alkanes	32.1	26.5	25.7	21.3
Alkenes	21.8	22.5	18.4	18.0
Aldehydes	14.4	17.7	29.4	33.8
Total (ppb)	468.8	169.0	463.4	168.1

[a] VOC/NO_x = 10; no dilution; no NO_x control; no entrainment from aloft; no emissions

[b] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.40 ppm (Table 8).

[c] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.12 ppm (Table 8).

for both mechansims under pre- and post-control conditions using VOC mixtures 1 and 4. Recall that VOC mixture 4 includes 9.5% aldehydes and that the ratio of the other species are the same as for VOC Mixture 1 (Table 4). The ratio of percent of NO to NO_2 conversions attributable to aldehydes using mixture 4 to that using mixture 1 is the same for both the ERT and the CBM mechanisms. However, as was the case when we compared VOC mixtures 1 and 2, the percent NO to NO_2 conversions attributable to aromatics increase in post-control conditions over pre-control conditions for the ERT mechanism and remains nearly constant for the CBM mechanism. Therefore, it appears that the ERT mechanism is most sensitive to an increase in aldehyde content because the aromatic and alkane concentrations are decreased.

4.2 VOC/NO_x Ratio

We saw in Section 3.2 that when the VOC/NO_x ratio was changed from 10 to 6 with VOC mixture 1, the PW and CBM mechanisms were most and least sensitive, respectively. Table 32 gives the percent NO to NO_2 conversions attributable to each organic class as well as the total number of NO to NO_2 conversions for these two mechanisms under pre- and post-control conditions at VOC/NO_x ratios of 10 and 6. For the CBM mechanism we see that the total number of NO to NO_2 conversions expressed as a concentration is about the same at VOC/NO_x ratios of 10 and 6; 467.8 ppb vs. 486.2 ppb for pre-control conditions and 168.9 ppb vs. 218.7 ppb for post-control conditions. In contrast, the total number of NO to NO_2 conversions for the PW mechanism depends strongly on the VOC/NO_x ratio; 519.0 vs. 635.9 ppb for pre-control conditions and 191.0 ppb vs. 334.7 ppb for post-control conditons. This increase in the total number of NO to NO_2 conversions with decreasing VOC/NO_x ratio is a result of the reactivity weighting scheme for determing initial VOC concentrations. As discussed in Part II, the potential for

Table 32. Percent of Total NO to NO_2 Conversions Due to Each Organic Class Using Initial VOC/NO_x Ratios of 10 and 6 for the PW and CBM Mechanisms[a]

Organic class	VOC/NO_x = 10 pre-control[b]	VOC/NO_x = 10 post-control[c]	VOC/NO_x = 6 pre-control[b]	VOC/NO_x = 6 post-control[c]
PW Mechanism				
Aromatics	28.1	26.5	26.4	31.3
Alkanes	31.2	21.9	27.5	20.3
Alkenes	32.4	39.4	36.3	35.1
Aldehydes	8.2	12.3	9.8	13.2
Total (ppb)	529.0	191.0	635.9	334.7
CBM Mechanism				
Aromatics	31.7	33.3	31.2	33.3
Alkanes	32.1	26.5	32.7	25.4
Alkenes	21.8	22.5	21.5	23.0
Aldehydes	14.4	17.7	14.6	18.3
Total (ppb)	467.8	168.9	486.2	218.7

[a] VOC mixture 1; no dilution; no NO_x control; no entrainment from aloft; no emissions

[b] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.40 ppm (Table 10).

[c] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.12 ppm (Table 10).

converting NO to NO_2 is much greater when reactivity weighting is used than when it is not. Because, at higher VOC/NO_x ratios, the total number of NO to NO_2 conversions is limited by the NO_x available, the effect of reactivity weighting is smaller.

4.3 Base Case Ozone

Predicted VOC control was found to be most sensitive to a change in the base case ozone for the DEM mechanism and least sensitive for the CBM mechanism. Table 33 gives the percent NO to NO_2 conversions attributable to each organic class for both mechanisms at base case ozone concentrations of 0.40 and 0.24 ppm. The most notable difference between the two mechanisms is that the percent of NO to NO_2 conversions attributable to alkenes is greater at post-control conditions than at pre-control conditions (31.5% vs. 39.9%) for the DEM mechanism, whereas for the CBM mechanism this percentage is roughly the same under pre- and post-control conditions (21.8% vs. 22.5%). The explanation for this behavior lies in the treatment of alkene chemistry by the two mechanisms. In the DEM mechanism, the alkene chemistry is more sensitive to the ozone concentration because the alkene-ozone reaction gives two peroxy radicals rather than a Criegee intermediate. Because ethene is lumped with the other alkenes, the rate constant for this reaction is higher than if ethene is treated separately. Thus, the effect is intensified.

4.4 Entrainment of VOC

Control predictions were found to be most sensitive to the entrainment of VOC from aloft (Consider the "mid-range" VOC mixture from Table 6) for the DEM mechanism and least sensitive for the Dodge mechanism. The CBM mechanism also exhibits a relatively low sensitivity to this VOC entrainment. Table 34 gives the number of NO to NO_2 conversions attributable to each organic class and the total number of NO to NO_2 conversions with and without entrainment. From

Table 33. Percent of Total NO to NO_x Conversions Due to Each Organic Class Using Base Case Ozone Concentrations of 0.40 and 0.24 ppm for the DEM and CBM Mechanisms[a]

Organic Class	Base Case O_3 = 0.40 ppm pre-control[b]	Base Case O_3 = 0.40 ppm post-control[c]	Base Case O_3 = 0.24 ppm pre-control[d]	Base Case O_3 = 0.24 ppm post-control[c]
DEM Mechanism				
Aromatics	27.2	26.1	27.2	28.4
Alkanes	30.5	21.5	31.6	26.0
Alkenes	31.5	39.9	30.1	36.3
Aldehydes	10.8	12.5	11.1	9.3
Total (ppb)	498.6	181.1	220.4	106.5
CBM Mechanism				
Aromatics	31.7	33.3	32.3	33.2
Alkanes	32.1	26.5	31.8	29.1
Alkenes	21.8	22.5	21.4	21.6
Aldehydes	14.4	17.7	14.5	16.1
Total (ppb)	467.8	168.9	232.6	100.9

[a] VOC mix 1; VOC/NO_x = 10; no dilution; no NO_x control; no entrainment from aloft; no emissions.

[b] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.40 ppm (Table 12).

[c] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.12 ppm (Table 12).

[d] VOC concentration (ppmC by volume) when maximum ozone concentration is 0.24 ppm (Table 12).

Table 34. Percent of Total NO to NO_2 Conversions Due to Each Organic Class With and Without Entrainment of VOC from Aloft for the DEM, Dodge and CBM Mechanisms[a]

Organic class	No entrainment		VOC entrainment	
	pre-control[b]	post-control[c]	pre-control[b]	post-control[c]
DEM Mechanism				
Aromatics	26.6	27.3	25.3	24.8
Alkanes	32.5	25.5	31.7	24.7
Alkenes	30.0	35.4	29.4	33.5
Aldehydes	10.8	11.8	13.6	16.9
Total (ppb)	295.1	163.5	298.6	159.9
Dodge Mechanism				
Aromatics	21.6	21.6	21.6	21.6
Alkanes	59.2	59.2	59.2	59.2
Alkenes	10.6	10.6	10.6	10.6
Aldehydes	8.6	8.6	8.6	8.6
Total (ppb)	376.1	215.2	368.6	219.0
CBM Mechanism				
Aromatics	31.8	32.9	30.6	29.2
Alkanes	32.4	30.1	31.2	27.9
Alkenes	21.4	21.3	20.9	19.3
Aldehydes	14.4	15.6	17.3	23.5
Total (ppb)	295.6	159.8	292.0	154.2

[a] VOC mix 1; VOC/NO_x = 10; no NO_x control; 0.05 ppmC VOC mid range mix entrained from aloft; no emissions; increase in mixing height from 250 to 1235m using the OAQPS characteristic curve.

[b] VOC concentration (ppbC by volume) when maximum O_3 concentration is 0.24 (Table 18).

[c] VOC concentration (ppbC by volume) when maximum O_3 concentration is 0.12 (Table 18).

this table it is seen that the olefin chemistry in the DEM mechanim causes it to be most sensitive to VOC entrainment. Note that as we found in section 4.3 the percent of NO to NO_2 conversions attributable to alkenes is greater at post-control conitions than at pre-control conitions for the DEM mechanism, whereas for the CBM mechanism this percentage is roughly the same under pre- and post-control conditions. The entrainment of VOC has the least effect on the Dodge mechanism because it is generally the "least reactive" of the mechanisms studied.

4.5 Entrainment of Ozone

We found in Section 3.9 that the DEM mechanism is most sensitive to the entrainment of ozone from aloft and the CBM mechanism is least sensitive. Table 35 gives the percentage of NO to NO_2 conversions attributable to each organic class with and without ozone entrainment. As we saw in Section 4.3, the percent of NO to NO_2 conversions attributable to alkenes increases from pre- to post- control conditions for the DEM mechanism due to the treatment of alkene-O_3 chemistry in that mechanism.

Table 35. Percent of Total NO to NO_2 Conversions Due to Each Organic Class with and without Entrainment of Ozone from Aloft for the DEM and CBM Mechanisms[a]

Organic class	No entrainment		Ozone entrainment	
	pre-control[b]	post-control[c]	pre-control	post-control[c]
DEM Mechanism				
Aromatics	26.6	27.3	26.4	26.8
Alkanes	32.5	25.5	33.2	24.3
Alkenes	30.0	35.4	29.6	37.1
Aldehydes	10.8	11.8	10.8	11.7
Total (ppb)	295.1	163.5	227.8	92.9
CBM Mechanism				
Aromatics	31.8	32.9	31.7	32.4
Alkanes	32.4	30.1	32.4	27.7
Alkenes	21.4	21.3	21.5	22.4
Aldehydes	14.4	15.6	14.5	17.5
Total (ppb)	295.6	159.8	217.9	84.2

[a] VOC mix 1; VOC/NO_x = 10; no NO_x control; 0.08 ppm O_3 entrained from aloft; no emissions; increase in mixing height from 250 to 1235m using the OAQPS characteristic curve.

[b] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.24 (Table 24).

[c] VOC concentration (ppmC by volume) when maximum O_3 concentration is 0.12 (Table 24).

5. SUMMARY AND RECOMMENDATIONS

We have examined the sensitivity of predicted VOC control requirements to the choice of chemical mechanism and to the variation of parameters associated with the chemical and meteorological nature of the atmosphere. Each chemical reaction mechanism was found to respond to a variation of the parameters in a somewhat different way; in many cases the relative sensitivity of the mechanism can be explained from an analysis of the intrinsic chemical features of the mechanism. Table 29 summarized the sensitivity calculations carrried out, including the mechanisms most and least sensitive to each variation. The sensitivity calculations can be summarized concisely as follows:

Initial VOC Composition

The choice of chemical mechanism has a large effect on VOC control predictions and on the sensitivity of the predicitions to a change in VOC composition. The ERT mechanism is most sensitive to a change in composition; the CBM least sensitive.

Aldehyde Content

Predicted VOC control is quite sensitive to the aldehyde content of the initial VOC mixture. Generally, the ERT mechanism exhibits the greatest sensitivity to changes in aldehyde content.

VOC/NO_x Ratio

The VOC/NO_x ratio was generally the parameter having the greatest influence on VOC control predictions. Generally, the ERT mechanism showed the greatest sensitivity to a change in the VOC/NO_x ratio, and the CBM exhibited the least sensitivity. In addition, the sensitivity of predictions to a change in the VOC composition is greatest at low VOC/NO_x ratios.

Base Case Ozone

Effects of changes in VOC composition are more pronounced the lower the base case ozone. The DEM mechanism is most sensitive to the choice of base case ozone.

Dilution

Differences among the predictions of the mechanisms are somewhat smaller at higher dilution rates than they are at low dilution rates.

Emissions

When emissions are assumed to be present, a given percent VOC reduction represents a larger reduction in total VOC in the atmosphere than in the absence of emissions.

VOC Entrainment from Aloft

Predicted VOC control requirements change by between 4 and 21% percent when VOC entrainment from aloft is included, regardless of the reactivity of the mixture assuming a base case ozone concentration of 0.24 ppm, and between 6 and 40% when a base case ozone concentration of 0.18 is assumed.

Ozone Entrainment from Aloft

All mechanisms exhibit a strong sensitivity to ozone entrainment from aloft. Ozone aloft is therefore a key variable in control studies. The sensitivity of VOC control to the VOC/NO_x ratio is influenced more by the entrainment of VOC than by the entrainment of ozone.

Initial HONO

Predictions obtained with the ERT mechanism are most sensitive to initial HONO; predictions from the PW mechanism are least sensitive.

In addition to determining the sensitivity of input parameters and choice of chemical mechanisms on VOC control requirements, we were able to explain the sensitivity of certain mechanisms to certain input parameters by using counter-species analysis to determine the number of NO to NO_2 conversions attributable to

each VOC class.

The results obtained in the series of reports of which this is the third paint a consistent picture of the behavior of chemical reaction mechanisms for photochemical smog. Several key issues emerged that are suggestive of future work:

(1) In much of the existing laboratory smog chamber data base, chamber wall effects are important enough to make accurate discrimination among rival chemical reaction mechanisms difficult. Continuing extensive analysis of data from outdoor chamber facilities is recommended as these systems seem to be characterized by smaller wall effects than indoor facilities.

(2) We have found that predicted VOC control requirements are highly sensitve to the assumed VOC/NO_x ratio and the VOC composition of the initial mixture and emissions. Therefore, it is important that these variables be as accurately characterized as possible for areas for which control strategies are to be designed.

(3) Because predicted VOC control can be quite sensitive to entrainment from aloft, the organic and especially the ozone concentration of entrained air aloft must be better characterized in areas where control strategies are to be designed.

(4) Continued effort should be placed on the evaluation of the performance of chemical reaction mechanisms in simulating both laboratory and outdoor smog chamber experiments. These experiments should include a wide range of conditions in order to gain a better understanding of the effects of input parameters (for example, initial VOC/NO_x, emissions and initial VOC composition) on control predictions.

(5) When determining control strategies, regulatory agencies should use several chemical mechanisms because at this time it is impossible to determine which chemical mechanism best simulates atmospheric chemistry.

(6) It is most important to know the input parameters as accurately as possible since the sensitivity of one input parameter may depend on the values assumed for other input parameters.

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